



Ash transformation in suspension fired boilers co-firing coal and straw

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Appendix D. Potassium capture by kaolin and fly ash powder in an entrained flow reactor

Final report, PSO-Eltra 4766: Ash transformation in suspension fired boilers co-firing coal and straw

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Potassium capture by kaolin and fly ash powder in an entrained flow reactor

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Abstract

To study the influence of local conditions on the reaction between gaseous KCl and kaolin or coal fly ash experiments were done on CHECs electrically heated entrained flow reactor, which can simulate the local conditions in suspension fired boilers. The experimental results were compared with model calculations to support the interpretation. The extent of the reaction between KCl vapor and coal minerals was evaluated by the amount of formed water insoluble potassium in the product. The effects of reaction temperature, residence time and potassium load on the potassium capture by coal minerals were studied. Due to not completely well controlled conditions during the experiments only preliminary conclusions can be provided. For experiments done at 1100° C with a molar ratio of K/Si=0.3 and a residence time of 1.07s approximately 80% of potassium from KCl reacted with kaolin. A changed temperature (1100-1300 ° C) or a changed amount of KCl (K/Si = 0.1 – 0.34) did only change the KCl conversion slightly. Si and Al rich coal ash seems to be less efficient to react with KCl compared to kaolin. However the applied coal ash had a larger particle size ($d_{50} = 22\mu\text{m}$) compared to the kaolin ($d_{50} = 10\mu\text{m}$).

Keywords: Potassium; Coal minerals; Pulverized fuel; Coal/straw co-firing

1. Introduction

Straw has been widely used for energy production in some countries including Denmark for many years. Nevertheless, straw is a somewhat challenging fuel for co-combustion, as it has high potassium and chlorine content [1, 2]. Previous studies have shown that there are strong interactions between K and Cl from straw and coal ash during co-firing [1, 3-6]. Control of the rate of deposit formation in biomass combustion is associated with the reactions between compounds that contain chlorine, alkali, sulfur, aluminum and silicon. High-risk chlorine compounds are in the form of KCl or NaCl. These alkali chlorides can react with sulfur and aluminum silicate compounds releasing HCl to the flue gas and forming sulfates and water insoluble aluminosilicates. It is imperative to get a better understanding of these reactions in order to obtain the benefits of straw and coal co-firing by appropriately choosing of coal type, straw share and optimal operation conditions.

Capture of alkali vapor by different sorbents has been extensively studied using thermal gravimetric analyzers and fixed-bed reactors [7-10]. However, these studies focused on alkali removal at temperatures below 900°C and the applied alkali was mainly sodium. In pulverized fuel boiler the ash particles are dispersed in the gas and the maximum flame temperature is about 1300-1700°C. There are some disadvantages of the thermal gravimetric analyzers and fixed-bed reactors. The heating rates of sorbents in such scale reactors are much slower than that of a practical combustor, where the heating rate is in the order of 10^4 - 10^5 °C/s [11]. Particles in fixed bed setups are stationary and continuously exposed to fresh flue gas, therefore the flow, the heating and mixing characteristics of a suspension combustor are unobtainable. The applied size of the sorbent particles in fixed bed systems is normally larger than 500 µm due to problems of high pressure drop over the sorbent bed and difficulties related to the formation of a well defined packed [10]. Therefore the internal pore diffusion resistance can not be neglected and the intrinsic rate constant of alkali capture at high temperatures are difficult to obtain.

There are only few studies on sodium capture by coal minerals in a drop tube furnace, which can be used to simulate the environment of high temperature thermal reactors such as suspension fired boilers [12, 13].

Kaolin is a common clay mineral and often present in coal. It has been shown that the extent of reaction between alkali and coal clay minerals, particularly kaolin, has important implications for the reduction of troublesome volatile alkali compounds [9, 10]. In this work kaolin is chosen as a model coal mineral. It is difficult to uncouple partial effects of different operating parameters on the alkali capture in a combustor. To alleviate this problem, potassium capture by kaolin and a bituminous coal fly ash are investigated by feeding KCl/kaolin and KCl/fly ash mixtures in a laminar electrically heated entrained flow reactor (EFR) under well-defined conditions. The objective of this study is to investigate the rate of the reaction between KCl and alumina silicates at the short residence time and relatively high temperatures typical of suspension fired boilers.

2. Experimental

2.1 Experimental setup

All tests were conducted in a laminar entrained flow reactor which allows precise control of the experimental conditions. A schematic diagram of the reactor is illustrated in figure 1. Details about the reactor can be found elsewhere [7]. Briefly the flow reactor has an internal length of 2 m and an internal diameter of 79 mm, and can be electrically heated to a maximum wall temperature of 1500°C.

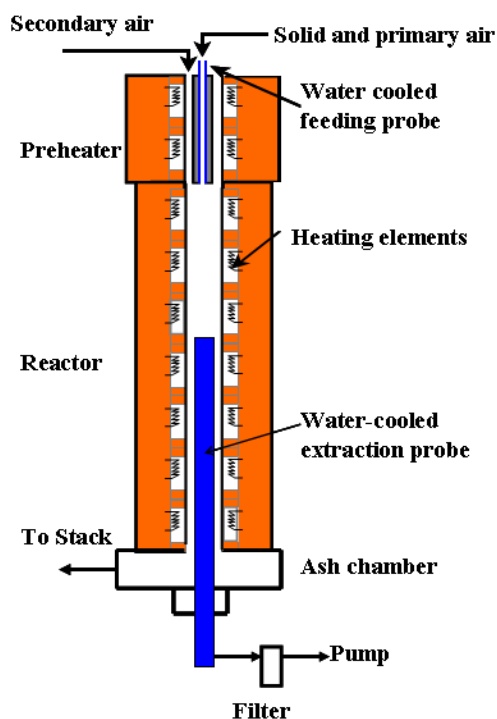


Figure 1. Sketch of the entrained flow reactor.

2.2 Potassium chloride evaporation test

Two methods of adding alkali compounds into a model coal ash are used in entrained flow reactor studies, namely, addition of fine alkali powders to the model coal ash [14] and wet impregnation of model coal ash in a solution of alkali compounds followed by drying, crushing and sieving [12, 13, 15]. Alkali salts containing potassium and sodium volatilizes upon combustion, becomes dispersed through the gas stream and may later react and condense on other ash particles. In this work the first method of potassium addition was applied by mixing KCl powders with kaolin and bituminous coal fly ash powders.

In order to quantify the amount of potassium vapor, evaporation tests of potassium chloride powders in the entrained flow reactor were conducted. Similarly to the evaporation tests conducted by Iisa et al. [16], the evaporated particles were collected by a cyclone with a cut diameter of about 2 μm and an aerosol filter with a polycarbonate filtration media which can collect particles above 0.05 μm . The reactor inlet gas was compressed air that passed through a silica gel dryer prior to the reactor. The feeding air

(supplying the solids) and total air flow is 10 NL/min and 60 NL/min, respectively. During the evaporation test experiments a KCl powder feed rate of 60 g/h, which was slightly larger than the typical KCl flow (50 g/h) in the kaolin/KCl mixture, was used to run smoothly without problem of automatic stop of the feeder. The applied sampling time was less than 10 min to avoid plugging of the sampling probe. Particles in the aerosol filter, cyclone, sampling pipe, water cooled extraction probe tip and inside the probe were collected. Pictures of the probe tip were taken to show the appearance of the collected KCl powders after evaporation at different temperatures. The amounts of the collected samples were compared with calculations, which were done by assuming the sampling flow has the same KCl concentration as the air flow in the reactor. The evaporation results were also compared with a model that simulates the heating and evaporation rate of the KCl particles.

2.3 Tests of KCl and mineral mixtures

Two tests series were conducted in this study. In the first series, tests were carried out at 900-1300°C without application of high temperature cleaning between experiments to remove the deposit on the reactor wall. To study the importance of the sulfation reaction, SO₂ gas was added to the desired S/Cl molar ratios in some of the experiments. The detailed test matrix is shown in table 1. The test matrix allows determination of the effects of reaction temperature, residence time, and potassium load on the interactions of potassium with kaolin and coal fly ash. The residence time of the particle was calculated from the distance between the reactor inlet and the top of the extraction probe and the average gas velocity over the cross section of the extraction probe. The average velocity was estimated from the volumetric flow rate assuming fully developed laminar flow in the reactor. Calculations show that the terminal velocities of the applied particles are very small and it is reasonable to assume no slip between the gas and the particles. Estimations of the particle heating time indicate that it can be assumed that the applied small particles achieve the temperature of the surrounding gas instantly (this is further discussed in section 3.1).

Previous straw/coal co-firing combustion tests showed that there is a clear correlation between the K/Si molar ratio in the fuel mixture and water soluble potassium content in the fly ash [3]. The fraction of potassium chloride in the mixture was added to obtain certain K/Si molar ratios, where a K/Si molar ratio of 0.34 corresponds to co-firing typical bituminous coal with 30 wt.% Danish straw. Different S/Cl molar ratios were applied by varying the amount of added SO₂.

Table 1. Test matrix.

Run	Mineral	K/Si (molar ratio)	Kaolin/KCl (molar ratio)	S/Cl (molar ratio)	Temperature (°C)	Residence time (s)
Series 1						
1	Kaolin	0.34	1.74	0	900	0.54
2	Kaolin	0.34	1.74	0	900	1.07
3	Kaolin	0.34	1.74	0	900	1.43
4	Kaolin	0.34	1.74	0	1100	1.07
5	Kaolin	0.34	1.74	0	1300	1.07
6	Kaolin	0.34	1.74	5.80	1100	1.07
7	Kaolin	0.34	1.74	5.80	1200	1.07
8	Kaolin	0.34	1.74	5.80	1300	1.07
9	Kaolin	0.34	1.74	9.30	1300	1.07
Series 2						
1	Kaolin	0.10	7.10	0	1100	1.07
2	Kaolin	0.18	3.50	0	1100	1.07
3	Kaolin	0.34	1.74	0	1100	1.07
4	Kaolin	0.34	1.74	0	1100	0.54
5	Kaolin	0.34	1.74	0	1100	0.77
6	Kaolin	0.34	1.74	0	1100	1.22
7	Kaolin	0.34	1.74	0	1200	1.07
8	Kaolin	0.34	1.74	0	1300	1.07
9	SAKLEI fly ash	0.34	-	0.01	1100	1.07
10	SAKLEI fly ash	0.34	-	0.01	1200	1.07
11	SAKLEI fly ash	0.34	-	0.01	1300	1.07

The potassium chloride powders were milled in a Retsch® ZM 100 centrifugal mill with a 80 µm sieve. Fine kaolin powders were mixed with KCl powders in appropriate proportion in a mixer for 3 h to ensure thorough mixing. Due to the color difference, big KCl particles were observed during the mixing with fly ash. To get better mixing, premixed KCl and fly ash are milled together through the mill with an 80 µm sieve.

The size distributions of the applied particles were analyzed by a Malvern laser diffraction particle size analyzer. The samples were dispersed in ethanol to avoid dissolving any water-soluble species that might be present. Figure 2 shows the measured particle size distributions of the applied powders. The D_{50} size of KCl, kaolin and SAKLEI fly ash powder are 26.29, 11.16, and 22.10 μm , respectively. Particle size distribution of KCl particles was also measured by a sieve for particles larger than 32 μm . The KCl particles easily agglomerate. Without plastic bricks on the sieve during the sieving, the KCl particles have a diameter of about 75 μm . While with plastic bricks on the sieve, the D_{50} of the particles is determined to 41 μm .

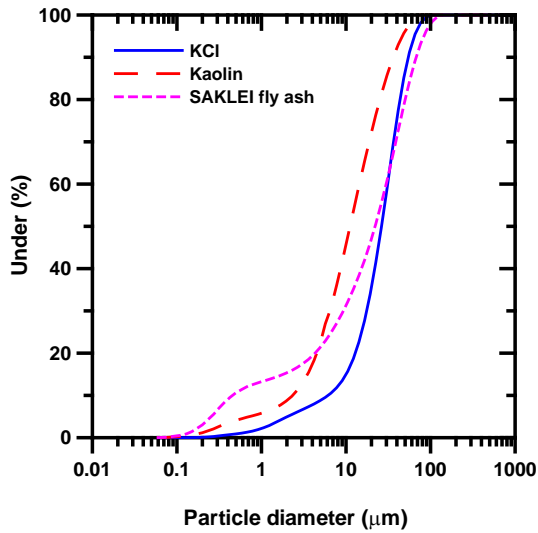


Figure 2. Particle size distribution of the applied powders, measured by Malvern laser diffraction analyzer.

Table 2 shows the chemical composition of the applied kaolin and SAKLEI fly ash. The Al and Si contents in kaolin and SAKLEI fly ash are nearly similar, while the SAKLEI fly ash has larger contents of Ca and Fe than kaolin.

Table 2. Composition of applied kaolin and bituminous coal SAKLEI fly ash. All in dry wt.%.

	Kaolin	SAKLEI fly ash
Si	22.75	23.42
Al	20.05	18.10
Ca	0.03	3.49
Mg	0.17	0.60
Fe	0.58	2.14
P	0.03	0.55
S	-	0.10
K	1.32	0.54
Na	0.03	0.11

Solid particles were fed into the reactor at a feed rate of 0.3 kg/h by a water-cooled air injection probe. In order to reduce the amount of added SO₂ gas a feed rate of 0.1 kg/h was applied in the sulfation tests. The applied carrier air and total air flow was 10 and 60 Nl/min, respectively, including about 2.5% water vapor which was obtained by passing the secondary air flow through a water bath. A vibrator was installed on the feeding probe to ensure smooth feeding of the particles. The reacted particles were collected by a water-cooled extraction probe with a metal filter which can collect particles larger than 1 µm.

The residence time was varied by changing the position of the extraction probe in the reactor. To avoid plugging of the extraction probe, after few trials the sampling time was chosen as 30 min for kaolin tests and 10 min for SAKLEI fly ash tests. To minimize the influence of previous deposits on the subsequent experiments, high temperature cleaning was applied in series 2 tests by increasing the reactor set points to 1400°C for 20 h after each test. This method was found to be effective to remove the deposit on the reactor wall. Samples collected in series 1 included particle from the metal filter and aerosol filter. In series 2, particles on the extraction probe tip, inside the extraction probe and pipes connecting the extraction probe and the metal filter were also collected.

2.4 Composition analysis of reacted samples

The collected samples were analyzed at Enstedværket laboratory, DONG Energy A/S. Total content of Al, Si, K and S were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The water soluble content of K, Cl and S were analyzed by ion-chromatography (IC). The total content of Cl was not analyzed since previous work showed that all the chlorine was water soluble [3].

The samples were first dried at 105°C for 2 h. For the analysis of total element concentration, about 50 mg sample was dissolved in a solution of 2 ml 30% H₂O₂, 6 ml concentrated HNO₃ and 1.65 ml 48% HF. Then the sample was decomposed in a microwave oven. After cooling the sample was mixed with 20 ml 4% boric acid and 10 ml pure water. Then the samples were heated in the microwave oven. After cooling the

solution was added to 100 ml by filling pure water and the ICP-OES analysis was performed. For the analysis of water soluble elements, about 50 mg and 100 mg sample was dissolved in 50 ml pure water, respectively. Then the sample bottle was closed and heated at 120°C for 1 h. After cooling the solution was filtered by using a 0.45 µm filter.

Selected samples were examined on an Oxford JEOL-JSM 5900 scanning electron microscope (SEM) to study the morphology. The energy-dispersive X-ray system was used for elemental analysis of individual particles with an acceleration voltage of 15 kV.

3. Results and discussion

3.1 Evaporation of potassium chloride powder

Evaporation tests were conducted at 200-1300°C. The test at 200°C was performed to study the dispersion and deposit behavior of KCl powders in the reactor. At such low temperature KCl hardly evaporates. Detailed evaporation results are shown in table 3. In all the tests the maximum KCl collection efficiency was about 42%. It is expected that a lot of KCl particles deposit on the reactor wall.

There is a significant increase of the amount of collected aerosols when the evaporation temperature increases from 200 to 1100°C as shown in table 3. The amounts of collected particles in the sampling pipe decreases with increasing the evaporation temperature, indicating that more fine aerosol particles are formed. We believe that the best estimation of the evaporation fraction is the ratio of aerosol to the sum of samples collected in the aerosol filter, the cyclone and the sampling pipe. This ratio shows that the KCl powder is only partly evaporated at 900° C (approximately 30%), while at 1100° C and above nearly all KCl is evaporated. The theoretical calculations indicate that the KCl is completely evaporated already at 900° C (see Figure 6). However, the calculations are based on a single particle size of 26 µm while in reality some particles are larger. Also an eventual poor mixing of particles and gas in the entrained flow reactor will delay the heating of the KCl particles.

Figure 3 shows the pictures of the sampling probe tip after KCl evaporation at different temperatures. The deposit on the probe tip increases with the evaporation temperature and time. The deposit fell down as flakes during cleaning instead of powders for the evaporation tests at temperatures above 1100°C. The sampling time was reduced from 10 min to 6 min to avoid plugging of the extraction probe for evaporation tests above 1100°C.

Table 3. Detailed results of KCl powder evaporation tests.

Temperature (°C)	200	200	600	900	900	900	1100	1100	1100	1200	1200	1300
Residence time (s)	1.07	2.67	1.07	1.07	1.07	1.07	0.54	1.07	1.22	1.07	1.07	1.07
Sampling duration (s)	600	600	600	600	600	600	600	509	360	360	360	360
Actual feed (g)	9.8	9.9	10.0	10.0	10.0	10.1	10.4	8.5	7.0	7.0	5.6	5.9
Calculated KCl concentration in the bulk gas (g/Nl)	0.016	0.017	0.017	0.017	0.017	0.017	0.017	0.017	0.019	0.019	0.016	0.016
Sampling flow (Nl/min)	14.830	15.017	14.269	16.320	16.499	17.400	11.414	16.710	15.502	15.905	15.722	16.165
Collected aerosol (g)	0.017	0.012	0.012	0.120	0.126	0.155	0.195	0.217	0.118	0.069	0.054	0.043
Collected cyclone sample (g)	0.000	0.001	0.000	0.018	0.014	0.029	0.000	0.002	0.000	0.000	0.000	0.000
Collected pipe sample (g)	0.134	0.079	0.127	0.317	0.313	0.311	0.005	0.008	0.011	0.001	0.000	0.000
Collected probe tip sample(g)	0.278	0.28	0.17	0.435	0.362	-	0.438	0.335	0.293	0.289	0.314	0.237
Collected inside probe sample (g)	0.176	0.176	0.131	0.244	0.222	-	0.175	0.17	0.097	0.09	0.075	0.063
Total collected sample (g)	0.605	0.548	0.44	1.134	1.037	-	0.813	0.732	0.519	0.449	0.443	0.343
Calculated sample collection from sampling flow and KCl concentration in bulk gas (g)	2.422	2.478	2.378	2.72	2.75	2.93	1.978	2.367	1.809	1.856	1.467	1.59
Collected sample/calculated collection (%)	24.98	22.12	18.5	41.69	37.71	-	41.09	30.92	28.7	24.2	30.19	21.58
Aerosol/total collected sample (%)	2.81	2.19	2.73	10.58	12.15	-	23.99	29.64	22.74	15.37	12.19	12.54
Aerosol/(aerosol+pipe+cyclone ash)(%)	11.26	13.04	8.63	26.37	27.81	31.31	97.50	95.59	91.47	98.57	100.00	100.00
Evaporation rate from model (%)				100	100	100	100	100	100	100	100	100

Note: Pipe samples are collected from the pipes connecting the extraction probe and the cyclone and aerosol filter.



200 °C, residence time: 1.07s, sampling time: 10 min



1100 °C, residence time: 1.22s, sampling time: 6 min



900 °C, residence time: 1.07s, sampling time: 10 min



1200 °C, residence time: 1.07s, sampling time: 6 min



1100 °C, residence time: 0.54s, sampling time: 10 min



1300 °C, residence time: 1.07s, sampling time: 6 min

Figure 3. Pictures of the extraction probe tip after KCl evaporation at different temperatures. Part of the sample fell down during removing of the probe for the 1200 °C test.

Iisa et al. measured the evaporation rate of 63-125 μm KCl particles in an entrained flow reactor [16]. Figure 4 illustrates the potassium vaporization at 900-1100°C as function of residence time. The amount of KCl vaporized was calculated on the basis of potassium detected in the collected aerosol particles. The amount of KCl vaporized increases with residence time and temperature. Generally, the observed KCl evaporation rate was small. They argued that the initial slow increase in the amount of vaporized K was due to the finite rate of heating of the particles. They estimated that the initial particle heating rate was only 3000-4000°C/s and it took about 0.2-0.3 s for the particles to reach the temperature of the reactor. The largest KCl evaporation rate was about 50%, which was obtained at 1100°C with a residence time of 1.2 s. This could be partly due to the relative larger particle size applied in their work.

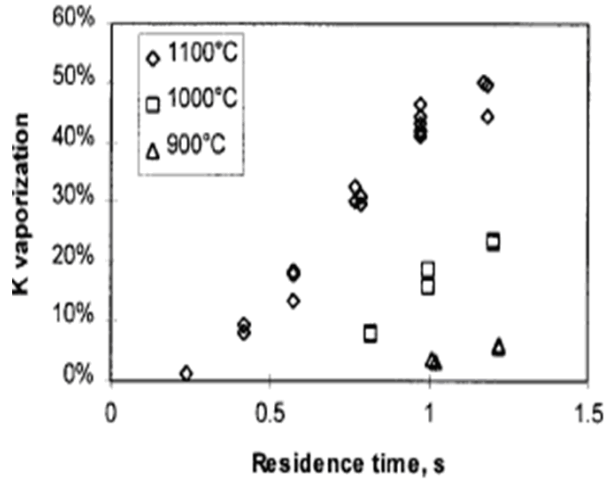


Figure 4. Potassium vaporization at 900-1100°C for KCl particles of 63-125 μm . After Iisa et al. [16]

To verify the measured KCl evaporation rate, simple calculations were conducted to estimate the complete evaporation time of a single KCl particle. The calculated evaporation time of a KCl particle included time for the particle to be heated to the gas temperature, time for particle melting and time for KCl evaporation through the gas-film. Detailed calculations can be found in appendix A. For a small particle with a diameter less than 100 μm , which is primarily heated by convective heat transfer, heating time increases linearly with the square of the particle diameter [11]. Figure 5 presents the required time for particles of different sizes to reach 99% of the gas temperature, which is 900°C. The heating time for a KCl particle of 26, 40 and 75 μm is 0.006, 0.013 and 0.046 second respectively. The average heating rate of the particle is in the range of 1.9×10^4 to

1.5×10^5 °C/s. This is in good agreement with the literature, where a typical heating rate of 10^4 to 10^5 °C/s is often observed [11].

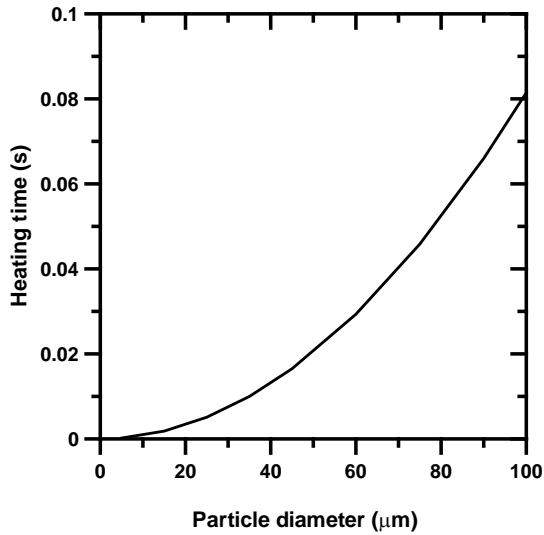


Figure 5. Time required for KCl particles in different sizes to reach 99% of the gas temperature (900 °C)

Due to the low KCl vapor pressure and short heating and melting time, the evaporations of KCl during the heating and melting stage are neglected. The decrease of particle temperature due to evaporation is taken into account by recalculating the KCl vapor pressure at lowered temperatures. Figure 6 shows the calculated evaporation rate of a 26 μm KCl particle at different temperatures as function of residence time.

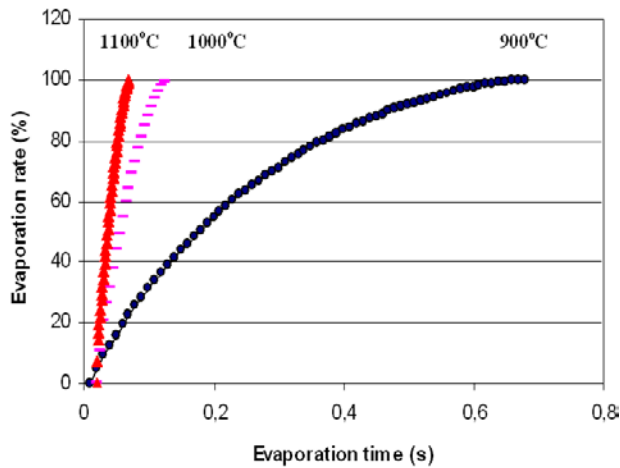


Figure 6. Calculated evaporation of a 26 μm KCl particle at different temperatures as a function of evaporation time.

There is large difference between the calculated and measured KCl evaporation rates. The calculations show however, that the evaporation rate is very sensitive to the particle size. When the KCl particle size is increased from 26 to 75 μm, the complete evaporation time at 900°C is increased from 0.68 to 6.68 s. Some agglomeration of the KCl particles was

observed during the sample preparation. So it is possible that the actual KCl particle size was larger than that measured by the laser diffraction particle size analyzer. The measured evaporation fractions (see Table 3) indicate that at 900°C the KCl particles are only partially evaporated, while at 1100 – 1300°C most of the KCl is present in the gas phase.

3.2 Results from first tests series

In this experimental series conducted on the entrained flow reactor the influence of changed temperature, reactor residence time and SO₂ addition were investigated. The reaction between potassium and kaolin can be evaluated by the amount of formed water insoluble potassium in the reacted sample. According to the reaction between metakaolin and KCl, water insoluble K₂O·Al₂O₃·2SiO₂ will be formed.

Figure 7 shows the effect of residence time on the chemical composition change of the reacted mixture. Detailed analysis results are given in table 4. The content of water insoluble K increases, while soluble K and Cl decrease with increasing the residence time. This might be due to both the larger rate of KCl evaporation and reaction between KCl vapor and kaolin at longer residence time. The particle residence time in a pulverized fuel boiler is in the range of 3-5 s. The water soluble K to Cl molar ratio in the reacted mixture is about 0.8-0.9, indicating that most of the water soluble K is in form of KCl.

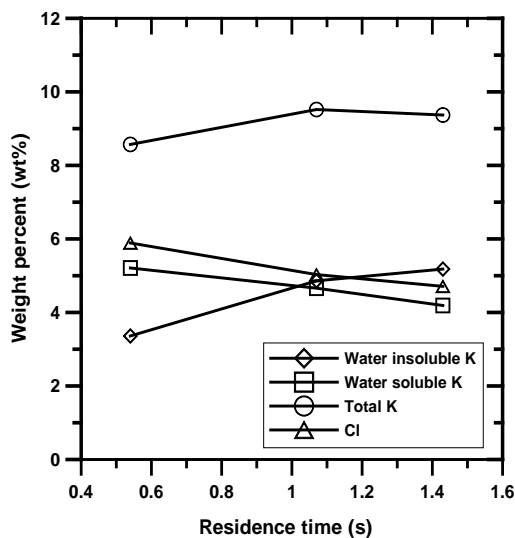


Figure 7. Effect of residence time on the composition change of the reacted samples. Kaolin powder is mixed with 14.24 wt% KCl ($K/Si=0.34$) and heated at 900 °C. The level of K and Cl in the input powder is respectively 8.6 and 6.8 wt%.

Table 4. Detailed analysis results of samples collected in series 1. All on dry basis. Input in the mixture: Al: 17,2 wt%; Si: 19,6 wt%; K from kaolin: 1,13 wt%; K from KCl: 7,47 wt%; Cl: 6,77 wt%. Applied operation conditions can be seen in Table 1.

Run No.	1	2	3	4	5	6	7	8	9
Total Al in collected sample (wt.%)	16.6	17.3	17.7	17.6	15.8	17.7	17.6	16.6	17.1
Total Si in collected sample (wt.%)	22.8	22.7	22.0	23.4	22.4	23.6	23.4	21.8	22.6
Total K in collected sample (wt.%)	8.57	9.52	9.37	9.26	11.71	8.00	9.11	12.35	10.85
Total S in collected sample (wt.%)						0.56	0.93	0.72	1.02
S-input from SO ₂ (wt.%)						35.45	35.45	35.45	56.85
Cl content in collected sample (wt.%)	5.49	5.03	4.71	3.30	4.56	1.64	1.09	3.94	2.89
Water soluble K in collected sample (wt.%)	5.21	4.66	4.19	2.85	4.01	2.35	2.21	5.59	4.65
Water soluble S in collected sample (wt.%)						0.37	0.79	0.70	1.03
Water insoluble K in collected sample (wt.%)	3.36	4.86	5.18	6.41	7.69	5.65	6.90	6.76	6.20
Water insoluble K/total K (wt.%)	39.07	56.51	60.23	74.53	89.41	65.69	70.36	68.93	63.22
Water soluble K/Cl molar ratio	0.86	0.84	0.81	0.78	0.80	1.30	1.84	1.29	1.46
Water soluble K/2S molar ratio						2.60	1.14	3.27	1.85
Water soluble K/(2S+Cl) molar ratio						0.87	0.71	0.92	0.82
Collected particle (g)	40.35	22.47	24.89	22.43	5.68	5.97	3.55	2.30	2.50
Calculated particle collection (g)	59.67	28.83	37.25	30.83	15.83	8.00	5.57	13.74	10.83
KCl conversion calculated from K content (%)	30.25	37.62	43.91	61.85	46.32	68.54	70.41	25.17	37.75
KCl conversion calculated from Cl content (%)	18.91	25.70	30.43	51.26	32.64	75.78	83.90	41.80	57.31

Note:

1. The elemental input in the mixture is calculated from the chemical analysis and weight fraction of kaolin.
2. Sulfur input from SO₂ is calculated from the added amount of KCl and the applied S/Cl molar ratio.
3. KCl conversion calculated from K content: $100\% \times (1 - \text{water soluble K in reacted sample} / \text{K input from KCl})$
4. KCl conversion calculated from Cl content: $100\% \times (1 - \text{Cl in reacted sample} / \text{Cl input from KCl})$

The effect of reaction temperature on composition change of the reacted mixture is illustrated in figure 8. The water insoluble K increases when the reaction temperature is increased. The contents of total K, water soluble K and Cl first decrease when the temperature increases from 900°C to 1100°C and then increase when the temperature further increases to 1300°C. However, the analysis result for test at 1300°C seems to be suspected. The detected total K content in the mixture reacted at 1300°C (11.71 wt%) is much larger than the input of K in the input mixture (8.60 wt%). The smaller water soluble K and Cl content at 1100°C compared to 900°C could be caused by the larger KCl evaporation and increased reaction between KCl vapor and kaolin at 1100°C.

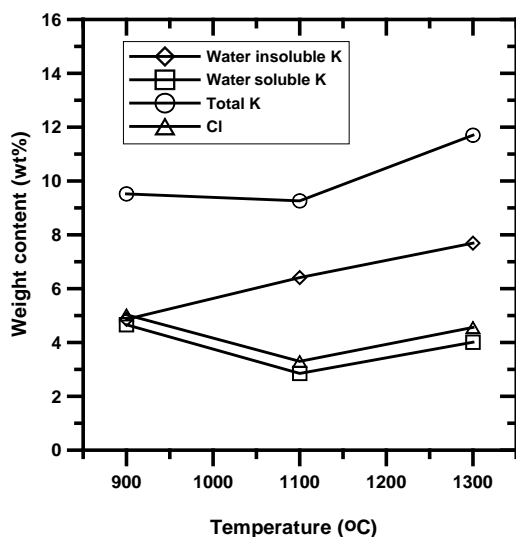


Figure 8. Effect of reaction temperature on the composition change of the reacted samples. Kaolin powder is mixed with 14.24 wt% KCl powder ($K/Si=0.34$) and heated for 1.07 s. The level of K and Cl in the input powder are respectively 8.6 and 6.8 wt%.

Figure 9 presents the influence of reaction temperature on the composition change of the reacted mixture with SO_2 addition. The total K content increases with reaction temperature. At 1300°C there are a lot of water soluble K and Cl in the reacted mixture. It is difficult to draw conclusion from these tests as uncertainty is observed in the test at 1300°. The total K content in the sample tested at 1300°C is 12.35 wt%, which is larger than the input of K (8.60 wt%) in the unreacted mixture. Almost all the detected sulfur is water soluble. The water soluble K to Cl and $K/(2S+Cl)$ molar ratios are about 1.3-1.8 and 0.7-0.9, respectively, indicating that most of the water soluble K is in the form of KCl and K_2SO_4 , and some sulfation reaction takes place. With SO_2 addition, the Cl content in the reacted mixture decreases from 3.30 wt% to 1.64 wt% for tests at 1100°C. The amount of water insoluble potassium compound is dependent on the competition between KCl reaction with kaolin and the sulfation reaction.

The experimental series one do have two important limitations. For the experiments at 900°C not all KCl were evaporated and therefore not available for reaction with kaolin. Also, the reactor was not adequately cleaned between experiments, and therefore some KCl is probably transported from the low to the high temperature experiments. It was therefore decided to only make experiments at 1100°C and above in experimental in series 2. Furthermore, the reactor was carefully cleaned of volatile ash species between experiments by heating it to 1400° C and flushes it with air.

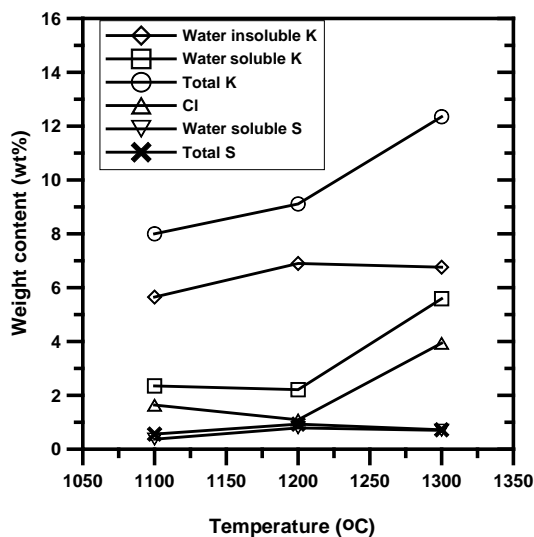


Figure 9. Effect of reaction temperature on the composition change of the reacted samples. Kaolin powder is mixed with 14.24 wt% KCl ($K/Si=0.34$) and heated for 1.07 s. SO_2 is added to an S/Cl molar ratio of 5.8.

3.3 Results from second tests series

In test series two are investigated the influence on changed residence time, K/Si ratio and temperature on the reaction of KCl with kaolin. Table 5 presents the mass balance for tests conducted in series 2. The amounts of collected samples are compared with a calculation that assumes the sampling flow has the same particle concentration as the main gas stream. In all the tests are collected from 90 to 120% of the calculated amount of collected sample. This indicates that a reasonable collection efficiency of the particles is achieved.

The mass balance of potassium can be evaluated by comparing the total K in the reacted samples with K in the unreacted mixture. Detailed chemical analysis results are given in appendix B. Figure 10 shows a comparison between measured K in the reacted sample and K input in the raw mixture. Generally the total potassium content in the reacted sample is reasonably similar to the K in the raw mixture.

Table 5. Mass balance for the second tests series. In experiment 1 to 8 is applied a KCl and kaolin mixture and in experiment 9 to 11 KCl and coal ash.

Run No.	1	2	3	4	5	6	7	8	9	10	11
Temperature (°C)	1100	1100	1100	1100	1100	1100	1200	1300	1100	1200	1300
KCl in mixture (wt.%)	3.91	7.63	14.24	14.24	14.24	14.24	14.24	14.24	17.15	17.15	17.15
K/Si molar ratio	0.10	0.18	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Residence time (s)	1.07	1.07	1.07	0.54	0.77	1.22	1.07	1.07	1.07	1.07	1.07
Actual feed (g)	147.5	145.6	150.7	149.7	151.2	149.9	151.5	151.0	50.8	51.2	64.2
Sampling flow (Nl/min)	5.352	3.683	14.895	2.373	9.752	9.854	5.505	4.867	4.535	6.568	3.467
Calculated particle concentration (g/Nl)	0.082	0.081	0.084	0.083	0.084	0.083	0.084	0.084	0.085	0.085	0.089
Particles collected in metal filter (g)	12.614	7.366	36.127	5.585	25.623	26.255	7.641	9.465	0.95	1.944	1.033
Particles collected in probe tip (g)	0.763	1.007	0.884	0.752	0.907	0.781	1.026	1.646	3.052	3.355	1.746
Particles collected inside probe(g)	1.205	1.620	0.303	0.143	2.360	0.435	4.000	3.145	0.588	0.524	1.549
Total collected sample(g)	14.582	9.993	37.314	6.480	28.890	27.471	12.667	14.257	4.590	5.823	4.328
Calculated particle collection from sampling flow and particle concentration (g)	13.156	8.937	37.412	5.921	24.575	24.619	13.899	12.248	3.840	5.604	3.709
Collected sample/calculated collection (%)	110.84	111.82	99.74	109.44	117.56	111.59	91.13	116.4	119.54	103.9	116.69

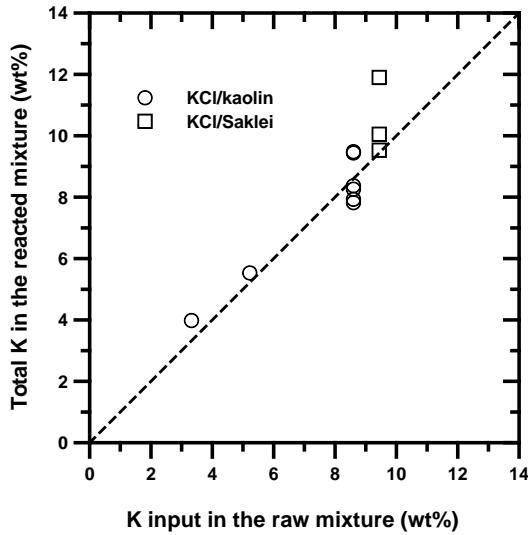


Figure 10. Total K content in the reacted mixture as function of K input in the raw mixture.

Figure 11 illustrates the ratio of water soluble K to total K in the reacted mixtures as function of K/Si molar ratio in the raw mixture. A low ratio of water soluble K to total K shows a high fraction of K appears as potassium alumina silicate. Results from some previous co-firing tests in the entrained flow reactor are also included for comparison [3].

There is observed a large difference between the results of the KCl/kaolin and the straw/coal test at a K/Si ratio of about 0.32-0.34. In contrast to the coal/straw co-firing tests, the ratio of water soluble K to total K in the reacted sample from KCl/kaolin tests seems not to change much with the K/Si molar ratio in the raw mixture (see data between the dotted lines). The results of the experiments with the coal ash/KCl mixture show that only a small fraction of the KCl has reacted with the coal ash.

The ratio of water soluble K to total K in the reacted KCl/kaolin mixture with K/Si=0.34 decreases when the reaction temperature increases from 1100 to 1300°C, showing that more water insoluble potassium is formed at 1300°C. For all the KCl/Saklei coal fly ash tests with K/Si=0.34, more than 76% of K is water soluble and in form of KCl. Presently it is not clear why the KCl not has reacted with the coal ash.

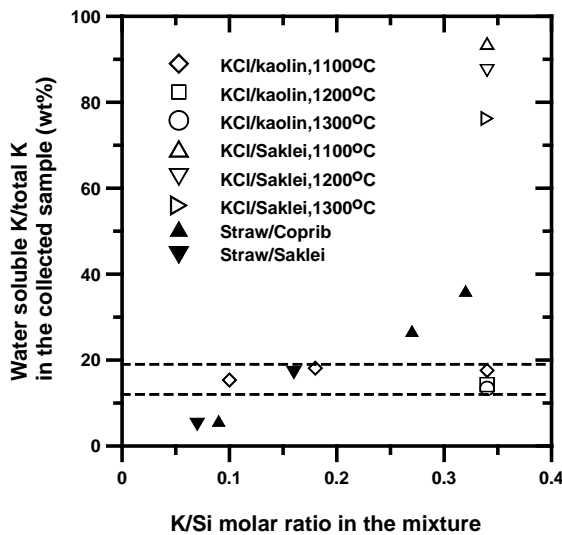


Figure 11. The ratio of water soluble K to total K in the reacted mixtures as function of K/Si molar ratio in the raw mixture.

Compared to the tests at 1100 and 1300°C in the first experimental series, the water soluble K contents in the second series are much smaller. This indicates that in the first series experiments some potassium might arise from deposits on the reactor wall deposited in previous tests. This confirms the necessity of applying high temperature cleaning between experiments.

Since the gaseous Cl is not measured, it is impossible to make an actual mass balance of Cl. However, comparison of the chlorine content in the reacted sample and the raw mixture shown in figure 12 shows how large the difference is between these two chlorine contents. Chlorine is detected in all the collected samples.

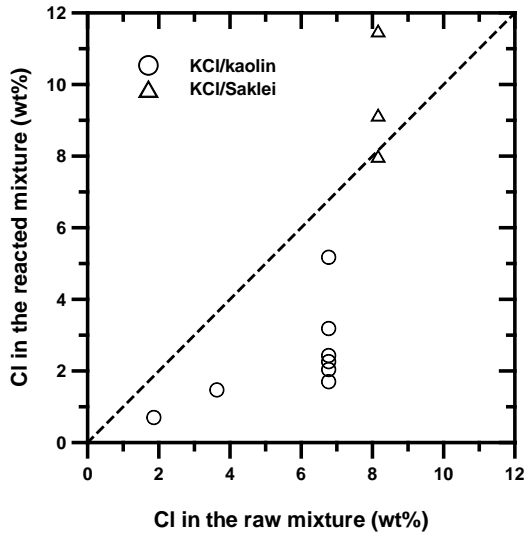


Figure 12. Comparison of chlorine content in the reacted mixture with chlorine input in the raw mixture.

There is a lot of chlorine in the reacted mixture from KCl/SAKLEI fly ash tests showing again that KCl do not have reacted with the coal ash. The detected Cl content in the reacted mixture is larger than Cl in the raw mixture. This might be partly due to the inhomogeneity of the analyzed sample. Only 50-100 mg sample is used for the analysis.

Figure 13 shows the chlorine content in the reacted mixture as a function of the K/(S+Si) molar ratio in the raw mixture. Data from previous straw/coal co-firing in the CHEC entrained flow reactor and full-scale boilers are also included for comparison. In Figure 13 it is seen that an increased availability of S and Si relative to K in the fuel mixture results in a decreased amount of Cl in the fly ash. The trend of the KCl/kaolin tests is slightly different from the co-firing tests in CHEC entrained flow reactor. The increase rate of Cl content in the reacted mixture as function of K/(S+Si) molar ratio in the raw mixture is somehow smaller for the KCl/kaolin tests compared to the coal/straw co-firing tests.

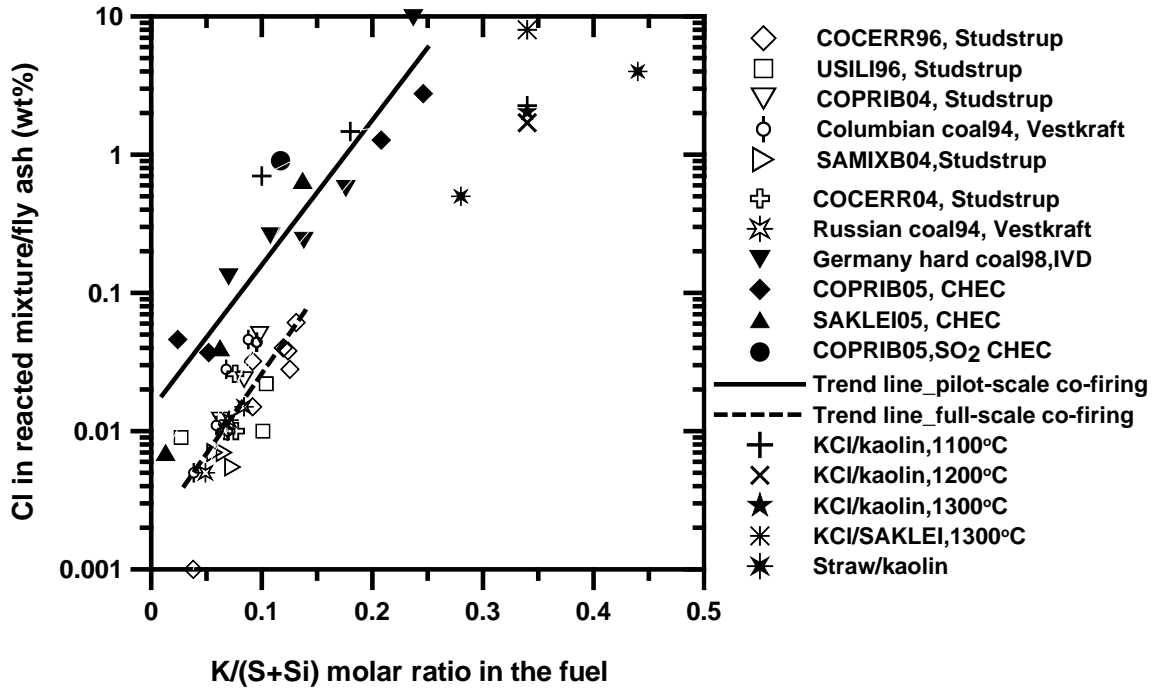


Figure 13. Chlorine content in the reacted mixture as a function of $K/(S+Si)$ molar ratio in the raw mixture. Data of straw/coal co-firing are from [3, 17-21].

In some previous experiments kaolin powders were added to straw and combusted in the entrained flow reactor at CHEC to investigate measures for minimizing deposit formation and corrosion during suspension firing of straw [22]. About 70 and 150 g kaolin powders were added to 1 kg straw and the corresponding K/Si molar ratio is 0.44 and 0.28, respectively. Deposit composition was analyzed and compared with the composition of deposit from straw combustion. The sulfur content in the straw was only about 0.2 wt% and the sulfation of the deposit can therefore be neglected. The results of chlorine contents in the deposit by adding kaolin to straw are included in figure 13 for comparison.

The effects of residence time on the total K, water soluble K, and Cl content in the reacted mixture are shown in the figure 14. Up to a residence time of 1.07s, the contents of water soluble K and Cl content in the reacted mixture decrease with increasing the residence time. The results indicate that increased residence time cause an increased conversion of KCl to potassium alumina silicate.

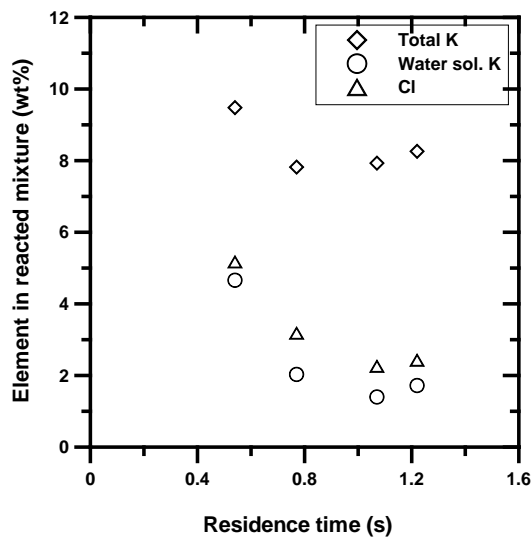


Figure 14. Potassium and chlorine content in the reacted KCl/kaolin mixture as function of residence time at 1100°C. (experiment 3-6)

Figure 15 shows the effect of reaction temperature on potassium and chlorine content in the reacted sample. The potassium and chlorine content hardly changes with the reaction temperature, when considering that the total potassium content in the sample tested at 1300°C is larger than that in the raw mixture. The total K content is expected to be similar for all mixtures tested at the different temperatures. It is seen that most K appear as potassium alumina silicates and the temperature do not seem to change that much.

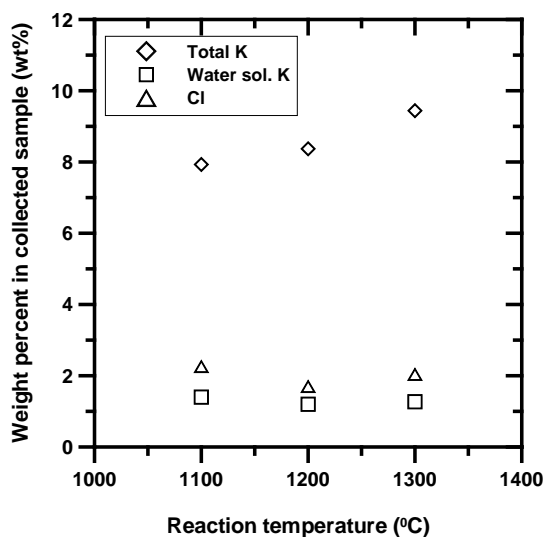


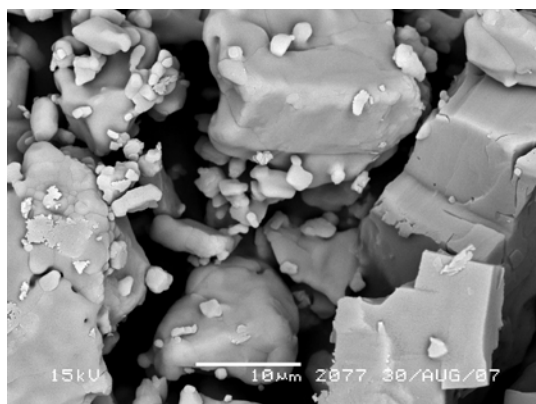
Figure 15. Potassium and chlorine content in the reacted KCl/kaolin sample as function of reaction temperature (experiment 3, 7, 8).

Experiments were also conducted with KCl/SAKLEI coal fly ash in temperatures from 1100 to 1300°C. However, nearly all potassium appeared as water soluble potassium in the collected samples, and it could be concluded that the coal ash did not react with the

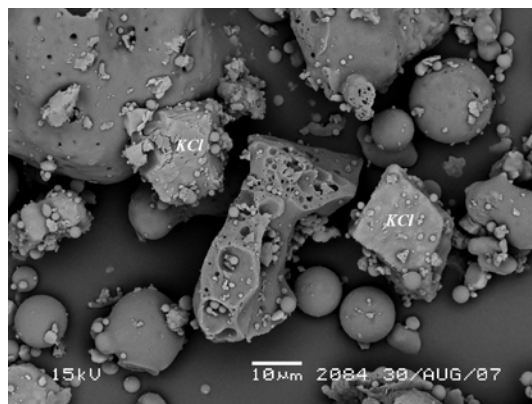
KCl. Presently it is not clear why only a limited reaction was observed. Previous test with SAKLAI coal and straw showed a high capability of the SAKLAI coal ash to bind potassium.

Detailed measuring data from both the SAKLAI and kaolin tests are shown in appendix B. Based on the potassium contents measurements it was calculated that in the KCl/kaolin tests between 73 and 84 % of the inlet potassium was converted to potassium alumina silicates in the cases with temperatures from 1100 to 1300°C and residence times of approximately 1.1 second.

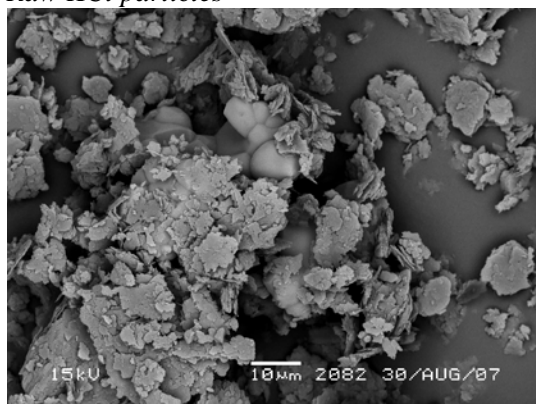
To improve our interpretation of the experiments SEM analysis were performed on both the raw and collected samples. Figure 16 presents the SEM images of the raw KCl, raw KCl/kaolin and KCl/SAKLEI fly ash mixture. Due to the much smaller density of KCl compared to kaolin, the KCl particles will appear as white in the backscattered electron image. SEM-EDX analyses also conform that the white particles are KCl. Single KCl particles with sharp edges can be found from the SEM image of the raw KCl powders. Cubic-like KCl particles are also observed among the many spherical particles in the KCl/SAKLEI fly ash mixture. The appearance of the KCl particles in the treated samples provides some information about the fate of the KCl. We believe that if the KCl particles are equal or smaller than 1 μm they are probably formed by condensation of non reacted gaseous KCl. Larger KCl particles, 10 μm or above, could indicate that some of the feed KCl is not evaporated in the entrained flow reactor.



Raw KCl particles



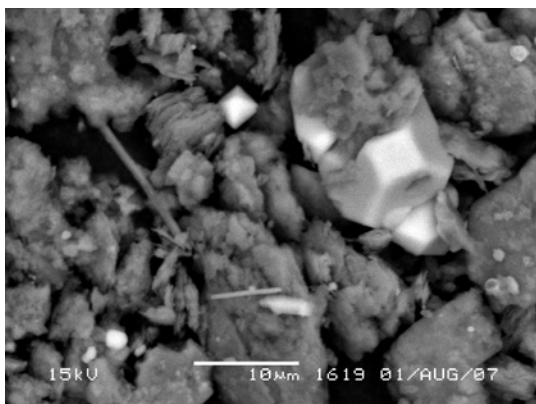
Raw KCl/SAKLEI fly ash mixture



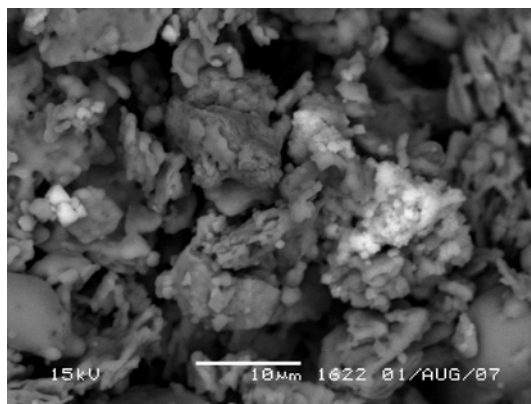
Raw KCl/kaolin mixture

Figure 16. SEM images of raw KCl, KCl/kaolin/SAKLEI fly ash mixture.

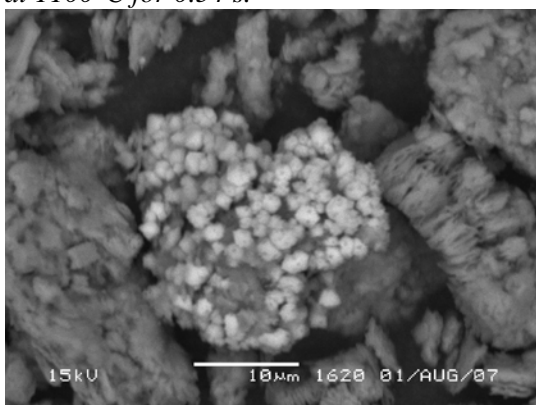
The SEM images of reacted KCl/kaolin and KCl/SAKLEI fly ash mixture are shown in figure 17. More SEM images and detailed SEM-EDX analysis results can be found in appendix C. Potassium chloride particles are observed in all the mixtures reacted at 1100-1300°C. In most cases the SEM images shows small KCl particles (<1 μm) or agglomerates of small particles. However, some cases of larger particles appear in the treated mixtures even up to samples exposed to 1200° C. Most large KCl particles are observed at 1100° C and a short residence time (0.54s). Why not all KCl was evaporated is not clear presently. It may be a poor mixture of gas and particles in the top of the reactor, it may simply be the largest particles that are not evaporated or it may be caused by an agglomeration of the raw KCl particles.



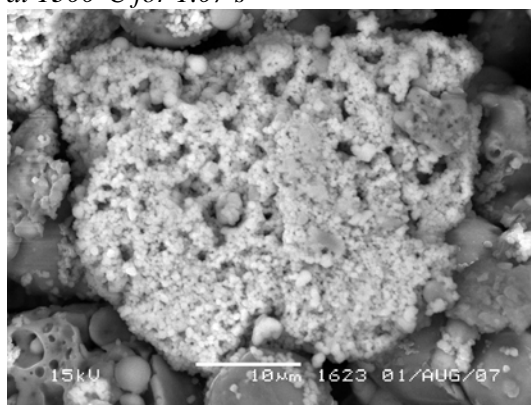
KCl/kaolin mixture with $K/Si=0.34$, reacted at 1100°C for 0.54 s.



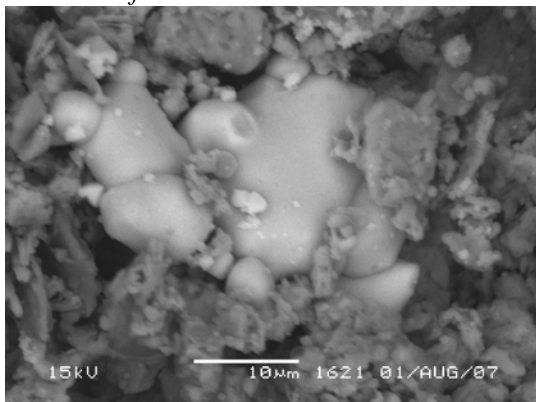
KCl/kaolin mixture with $K/Si=0.34$, reacted at 1300°C for 1.07 s



KCl/kaolin mixture with $K/Si=0.34$, reacted at 1100°C for 1.07 s.



KCl/SAKLEI fly ash mixture with $K/Si=0.34$, reacted at 1100°C for 1.07 s



KCl/kaolin mixture with $K/Si=0.34$, reacted at 1200°C for 1.07 s.

Figure 17. SEM images of reacted KCl/kaolin and KCl/SAKLEI fly ash mixtures.

Figure 18 shows SEM images of deposits from previous straw/kaolin combustion tests [22]. Two types of particles are observed in the deposit from straw combustion. There are some silica rich spheres with a size of 10-30 μm . The other small particles are KCl and K_2SO_4 which glue the big particles together or deposit on the surfaces of the big particles. The big particles in the deposit from straw/kaolin tests are rich in Al, Si and K. No non converted kaolin particles were observed.

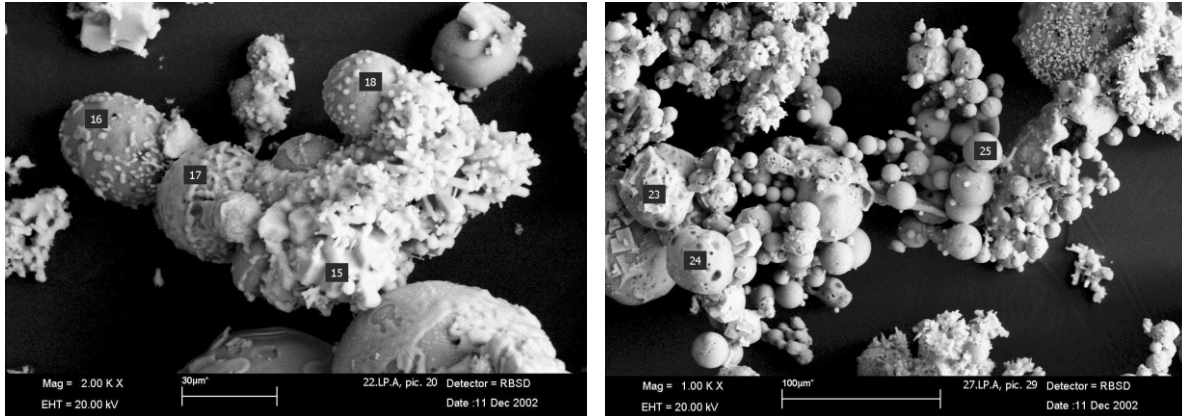


Figure 18. SEM images of deposit from straw/kaolin tests [22]. Left: pure straw; right: straw and kaolin.

Compared to the straw/kaolin combustion tests, the kaolin particles from KCl/kaolin tests appear as flakes rather than spheres. This is probably due to the lack of a flame and therefore a low temperature in the KCl/kaolin test compared to the combustion studies. The actual local flue gas temperature in the top of the reactor is probably in the range of 1400-1700°C during the combustion experiments [22]. Particles in the present KCl/kaolin test are much less melted than the combustion ash.

4. Model evaluation of parameters affecting potassium capture by kaolin in entrained flow reactor

Model simulations are conducted to investigate the effects of parameters, such as particle diameter, residence time, rate constant and particle KCl effective diffusion coefficient, on potassium capture by kaolin powder in the entrained flow reactor. The previously developed fixed-bed single particle model is extended to a plug flow model²³. In such a case kaolin powders are injected into a plug flow reactor and react with KCl vapor. The bulk KCl concentration is therefore updated for each small time step. The KCl conversion can be calculated from the single pellet conversion and the molar ratio of kaolin to KCl in the flow. A simple gas-film control and a kinetic control model are also developed to study the importance of external mass transfer and reaction kinetics on the potassium capture by kaolin powders. Detailed description of the models can be found in appendix D.

Since the previous developed fixed bed model²³ works only at a reaction temperature of 900°C, simulations of the plug flow reactor are conducted at 900°C using the rate constant and effective KCl diffusion coefficient from the fixed-bed single particle model, i.e. $k=3907 \text{ m}^3\text{-gas/m}^3\text{-solid/s}$, $D_e=4.5\text{E-}6 \text{ m}^2\text{/s}$. The calculated KCl concentration of KCl/kaolin mixture with K/Si molar ratio of 0.34 at 900°C is 3550 ppmv (14.24 wt% of KCl in the mixture, fed at a rate of 5 g/min to 60 Nl/min air). The corresponding kaolin to KCl molar ratio is about 1.74 and the d_{50} size of kaolin powders is about 10 μm .

Figure 19 presents the calculated initial KCl profile inside the kaolin particle. The KCl concentration is normalized with the initial KCl bulk concentration. A steep KCl profile is observed for large particles, on the other hand a flat profile is observed for small particles. The curves show that for large particle sizes intraparticle diffusion resistance is largely controlling the KCl capture rate, while for small particles the rate is under kinetic control.

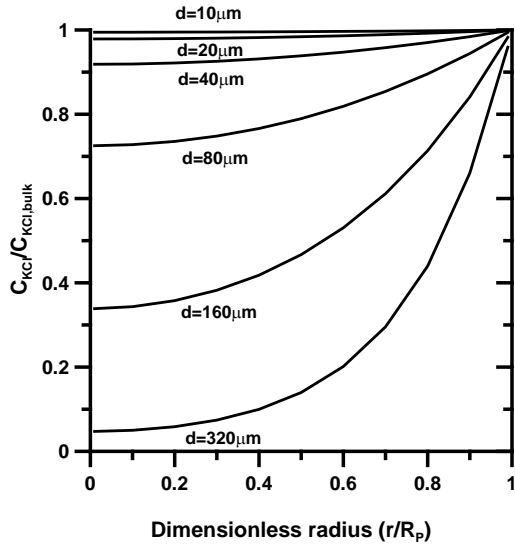


Figure 19. Initial KCl concentration profiles inside the kaolin particles at different particle sizes. $k=3907 \text{ m}^3\text{-gas/m}^3\text{-solid/s}$, $D_e=4.5E-6 \text{ m}^2/\text{s}$ (temp 900°C).

Figure 20 illustrates the calculated KCl conversion as a function of residence time for different particle sizes. The KCl conversions for particles smaller than $20 \mu\text{m}$ are very similar and this is in agreement with the initial KCl profile as shown in figure 19. When the particle diameter is smaller than $20 \mu\text{m}$ the intraparticle diffusion resistance can be neglected.

However the simulated KCl conversion using $10 \mu\text{m}$ kaolin particle is lower than that determined from chemical analysis of the reacted mixtures (See Figure 21). This shows that the rate constant for potassium capture by kaolin powders is not in agreement with the rate constant determined by using large kaolin pellets.

The KCl conversion in the entrained flow reactor test can be calculated from the Cl content in the reacted mixture and the Cl input or the water soluble K content in the reacted mixture and the K input. KCl conversions as a function of residence time at 900°C are shown in table 6. The KCl conversion calculated from Cl content is about 12% less than that calculated from K content. Since we know that not all KCl is present in the gas phase at 900°C the conversion values shown in Table 6 are minimum values.

Table 6. Calculated KCl conversions for entrained flow reactor tests at 900 °C.

Residence time (s)	KCl conversion from Cl content (%)	KCl conversion from K content (%)
0.54	18.91	30.25
1.07	25.71	37.62
1.43	30.43	43.91

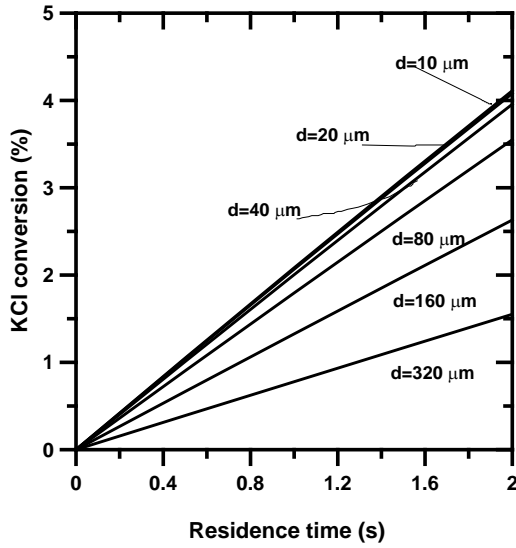


Figure 20. Simulated KCl conversion as function of residence time at 900 °C for different particle sizes. $k=3907 \text{ m}^3\text{-gas/m}^3\text{-solid/s}$, $D_e=4.5\text{E-}6 \text{ m}^2/\text{s}$, kaolin/KCl molar ratio=1.74.

To study the sensitivity of the calculated KCl conversion to rate constant values and effective KCl diffusion coefficient, simulations are carried out by arbitrarily changing the rate constant and the effective diffusion coefficient. Figure 21 shows the simulated KCl conversion using different rate constants. Also the measured conversion data at 900° C are shown in Figure 21. Using such a large rate constant (of $97675 \text{ m}^3\text{-gas/m}^3\text{-solids/s}$) the KCl conversion calculated from the K content in the mixture can be fitted.

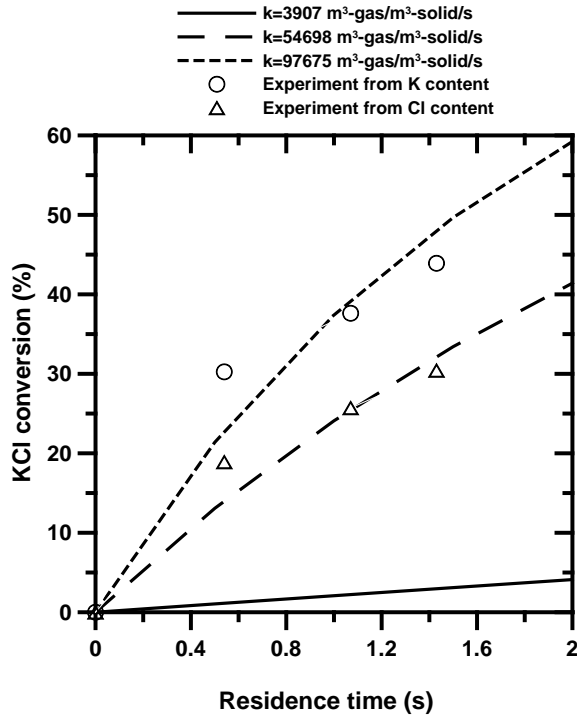


Figure 21. Sensitivity of KCl conversion to rate constant. Particle diameter=10 μm , $D_e=4.5\text{E-}6 \text{ m}^2/\text{s}$, Kaolin/KCl molar ratio=1.74.

The KCl conversion is less sensitive to the KCl effective diffusion coefficient, as presented in figure 22. This is in agreement with results shown in Figure 20 that demonstrated that for the 10 μm particles diffusion is not important. The parameters used in the original large particle fixed bed model²³ was $K = 3907 \text{ m}^3\text{-gas/m}^3\text{-solids}$ and $De = 4.5\text{E-}6 \text{ m}^2/\text{s}$.

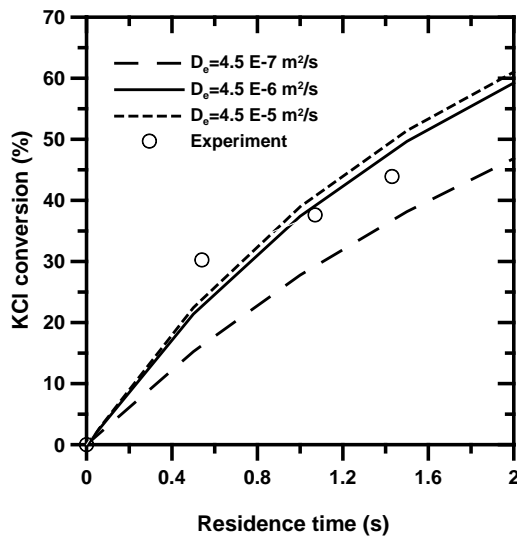


Figure 22. Sensitivity of KCl conversion to effective KCl diffusion coefficient. Particle diameter=10 μm , $k=97675 \text{ m}^3\text{-gas/m}^3\text{-solid/s}$, Kaolin/KCl molar ratio=1.74.

Figure 23 illustrates the simulated KCl conversion as function of residence time using an external gas-film control model (assuming indefinitely fast kinetics). Using a 80 μm kaolin particles more than 98% of KCl will be converted after 2 seconds. This indicates that the external mass transfer is fast and the gas film resistance for kaolin particles of the 10 μm applied in this work can be neglected.

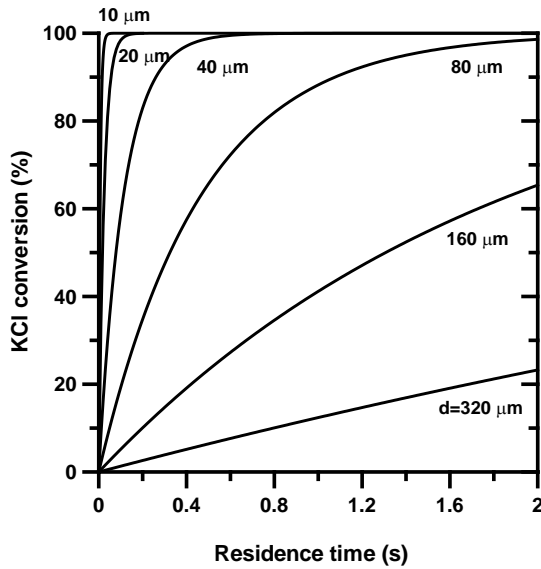


Figure 23. Simulated KCl conversion as function of residence time for different particle sizes. Gas film controlled model. Kaolin/KCl molar ratio=1.74

Simulated KCl conversion as function of residence time using a kinetic model is presented in figure 24 (no transport limitations is included). When the rate constant is 6 times larger than the rate constant from fixed-bed model the KCl conversion from K content analysis can be fitted. This again shows that the rate constant determined from fixed-bed experiments is smaller than the rate constant based on the entrained flow reactor tests using fine kaolin powders.

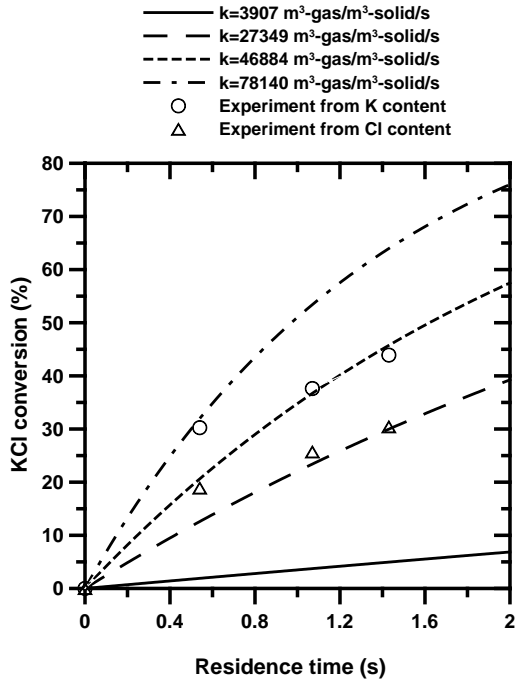


Figure 24. Calculated KCl conversion as function of residence time. Kinetic controlled model. Kaolin/KCl molar ratio=1.74.

5. Conclusions

To study the influence of local conditions on the reaction between gaseous KCl and kaolin experiments were done on CHECs electrically heated entrained flow reactor, which can simulate the local conditions in suspension fired boilers. The experimental results were compared with model calculations to support the interpretation. This part of the project work is preliminary in the sense that the model do not covers all the relevant temperatures and the experimental results do have some serious uncertainties.

The degree of KCl reaction with Kaolin in the entrained flow reactor experiments is determined by the fraction of water soluble K in the resulting particle product. Potassium reacted with kaolin forms potassium alumina silicates that are not water soluble. However, the concentration of gaseous KCl available for the reaction with kaolin can only be determined if all injected KCl is evaporated. Experimental tests indicated that nearly complete evaporation was obtained if the temperature was 1100° C or above. However, analysis of SEM images of the product from 1100° C experiments indicates that even here some KCl has not been completely evaporated. This may be caused by some larger KCl particles or by a bad mixing between the hot gas and the injected KCl/kaolin mixture.

However, with some precaution the following conclusions can be provided based on the experimental and modeling work:

- For particles below 20 μm the kinetics determine the conversion rate and both external and internal transport limitations are not important.
- For experiments done at 1100 ° C with a molar ratio of K/Si=0.3 and a residence time of 1.07s approximately 80% of potassium from KCl reacted with kaolin.
- A changed temperature (1100-1300 ° C) or a changed amount of KCl (K/Si = 0.1 – 0.34) did only change the KCl conversion slightly.
- Si and Al rich coal ash seems to be less efficient to react with KCl compared to kaolin. However the applied coal ash had a larger particle size ($d_{50} = 22\mu\text{m}$) compared to the kaolin ($d_{50} = 10\mu\text{m}$).
- The kinetic rate constant of the reaction of KCl with kaolin have been determined to be much larger for the entrained flow reactor experiments than the rate constant determined from fixed bed experiments on larger particles. Presently the reason for the observed deviation is not clear.

Acknowledgements

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Appendix A. Calculation of complete evaporation time for a 26 µm KCl particle

The evaporation time of a KCl particle includes time for the particle heated to the gas temperature, time for melting and time for evaporation through the gas-film (assuming that the KCl release during heating and melting is insignificant).

Time required for the particle to reach the gas temperature:

For a small particle with a diameter less than 100 µm, this is primarily heated by convective heat transfer. The heating time can be calculated by solving following equation:

$$T_p(t) = T_p(t=0) + (T_g - T_p(t=0))(1 - \exp(-t/\tau_H))$$

$$\text{where } \tau_H = \frac{\rho_p C_p d^2}{12 \lambda_g}, \rho_p = 1990 \text{ kg/m}^3, C_p = 966 \text{ J/kg/K}, \lambda_g = 0.09 \text{ W/m/K}$$

According to the above equation it takes infinite time for the particle to reach the gas temperature. Here the time required for the particle to reach 99% of the gas temperature is calculated.

Possible temperature decrease due to evaporation:

It is expected that the particle temperature could decrease due to the heat required for evaporation. The possible temperature change is estimated by following equation:

$$\dot{m} \Delta H_{eva} = h A \Delta T$$

where \dot{m} is the evaporation rate (kg/s), ΔH_{eva} is the heat of evaporation (J/kg), h is the heat transfer coefficient (W/m²-K), A is the particle outer surface area, ΔT is the decrease of particle temperature (K). For 26 µm KCl particle, the outer surface area is $A = 2.123 \times 10^{-9} \text{ m}^2$.

Evaporation heat of KCl:

NIST-JANAF thermochemical table shows that, the heat of KCl evaporation is 49.5 kcal/mol = 207.257 kJ/mol (2780107 J/kg).

Estimation of heat transfer coefficient through the particle surface:

The heat transfer coefficient can be calculated from the Nusselt number:

$$Nu = \frac{hd}{k} = 2 + 0.6 Re_p^{1/2} Pr^{1/3}$$

Re for 26 μm particle at 900°C:

The difference of the velocity between the gas and the particle is the particle terminal settling velocity. For particle with a size between 1-100 μm , it is reasonable to calculate the terminal setting velocity using the Stoke's law.

$$v = gd^2 \frac{(\rho_{KCl} - \rho_{gas})}{18\mu}$$

Where $\rho_{KCl}=1990 \text{ kg/m}^3$, $\rho_{gas}=0.301 \text{ kg/m}^3$, the viscosity of air at 900°C is $4.67\text{E-}5 \text{ kg/m/s}$:

$$v = gd^2 \frac{(\rho_{KCl} - \rho_{gas})}{18\mu} = 9.81 \times (26 \times 10^{-6})^2 \frac{(1990 - 0.301)}{18 \times 4.67 \times 10^{-5}} = 0.016 \text{ m/s}$$

$$Re_p = \frac{\rho_{gas} v d}{\mu} = \frac{0.301 \times 0.016 \times 26 \times 10^{-6}}{4.67 \times 10^{-5}} = 0.003$$

The heat capacity of air at 900°C is calculated from

$$C_p(T) = a + bT + cT^2 + dT^3 = 27.435 + 0.618 \times 10^{-2} T - 0.09 \times 10^{-5} T^2 = 33.45 \text{ J/mol/K}$$

Molar weight of air is: $0.79 \times 28 + 0.21 \times 32 = 28.84 \text{ g/mol}$, so the heat capacity of air at 900°C is 1159.85 J/kg/K . Heat conductivity k for air is about 0.076 W/m/K , then

$$Pr = \frac{C_p \mu}{k} = \frac{1159.85 \times 4.67 \times 10^{-5}}{0.076} = 0.713$$

This is in good agreement with the literature where typical Pr of air is in the range of 0.66-0.75.

$$Nu = \frac{hd}{k} = 2 + 0.6 \times 0.003^{1/2} \times 0.713^{1/3} = 2.028$$

The calculated Nusselt number is very close to 2. The calculated heat transfer coefficient is:

$$h = \frac{kNu}{d} = \frac{0.076 \times 2.028}{26 \times 10^{-6}} = 5928 \text{ W/m}^2/\text{K}$$

The calculated decrease of particle temperature due to evaporation at 900°C is:

$$\Delta T = \frac{\dot{m}\Delta H_{eva}}{hA} = \frac{2.73 \times 10^{-11} \times 2780107}{5928 \times 2.123 \times 10^{-9}} = 6.03 K$$

The calculated results for 900, 1000 and 1100°C are shown in following table. The evaporation rate is estimated from previous calculation without updating the temperature change due to evaporation. The temperature decrease is relative large at 1000 and 1100°C; as a result the saturated KCl vapor pressure becomes lower.

	900°C	1000°C	1100°C
Evaporation rate (kg/s)	2.73E-11	1.48E-10	3.73E-10
KCl particle density (kg/m ³)	1990	1990	1990
Air density (kg/m ³)	0.301	0.277	0.257
Air viscosity (kg/(m.s))	4.67E-5	4.91E-5	5.12E-5
Air heat capacity (J/(kg.K))	1159.85	1173.50	1186.67
Air heat conductivity (W/(m.K))	0.076	0.080	0.084
Initial particle setting velocity (m/s)	0.016	0.015	0.014
Initial Re _p	0.003	0.002	0.002
Pr	0.713	0.720	0.723
Initial Nu	2.028	2.026	2.023
Heat transfer coefficient (W/(m ² .K))	5928	6234	6536
ΔT (K)	6.03	31.08	74.73
Saturated KCl vapor pressure (pa)	576	2304	7308
Saturated KCl vapor pressure at temp-ΔT(pa)	525	1540	3146

Melting time of KCl particle:

The heat of KCl fusion is 26.28 kJ/mol (353515 J/kg). When the particle is melting, the temperature difference between the gas and the particle is constant, the melting rate at 900°C can be calculated from:

$$\dot{m}\Delta H_{fus} = hA\Delta T$$

$$\dot{m} = \frac{hA\Delta T}{\Delta H_{fus}} = \frac{5928 \times 2.123 \times 10^{-9} \times (900 - 771)}{352515} = 4.605 \times 10^{-9} \text{ kg / s}$$

The weight of a 26 μm KCl particle is about 1.831E-11 kg, complete melting time for the particle is 0.004 s. The melting time of a 26 μm KCl particle at 900, 1000 and 1100 °C are given in the following table. The particles completely melt in very short time.

	900°C	1000°C	1100°C
Melting time (s)	0.004	0.002	0.001

Evaporation rate as function of evaporation time:

As the particles have reached the gas temperature, vaporization proceeds at a rate which is limited mainly by mass transfer [22]. The mass transfer rate depends on the external surface area of the particles, which decreases with time as KCl is vaporized. The evaporation rate of a KCl particle with an initial diameter of 26 μm as function of time is calculated by considering the change of the particle weight, diameter with time. Due to the low KCl vapor pressure and short heating and melting time, the evaporations of KCl during the heating and melting stage are not calculated. The decrease of particle temperature due to evaporation is taken into account by recalculating the KCl vapor pressure at lowered temperatures.

The external mass transfer coefficient can be calculated from the Sherwood number:

$$Sh = \frac{k_m d}{D} = 2 + 0.6 Re_p^{0.6} Sc^{1/3}$$

$$Sc = \frac{\mu}{\rho D}$$

It is important to use the correct diffusion coefficient. Both the diffusion coefficients for nonpolar and polar gas have been used in literature to calculate the diffusion coefficient of KCl in nitrogen.

Comparison of calculated KCl diffusion coefficient (cm^2/s) using polar and nonpolar equations:

	900°C	1000°C	1100°C
Polar	1.2439	1.4627	1.6967
nonpolar	1.0992	1.2709	1.4521

The diffusion coefficient of KCl in nitrogen calculated using the polar equation is about 15% larger than that calculated using the nonpolar equations. Since KCl(g) is polar, the polar diffusion coefficient is used in the calculation.

Calculation procedure for KCl particle evaporation at given temperature:

1. The saturated vapor pressure of KCl is calculated and taken as the KCl concentration at the particle surface.
2. Calculate the particle terminal settling velocity, Re, Sh, Nu, mass transfer coefficient k, heat transfer coefficient and temperature decrease due to evaporation using the initial particle diameter, the particle initial weight, and surface area.
3. Calculate the weight loss of the particle after certain time (0.01 s) and evaporation rate $dm_{loss} = 0.07455kA(C_{KCl} - C_{KCl,bulk})dt$.
4. Recalculate the particle terminal settling velocity, Re, Sh, k, Nu, h, ΔT , particle diameter, particle weight and surface area, bulk KCl concentration.
5. Calculate the weight loss of the particle after certain time (0.01 s) and evaporation rate and continue the loop to complete evaporation of the particle.

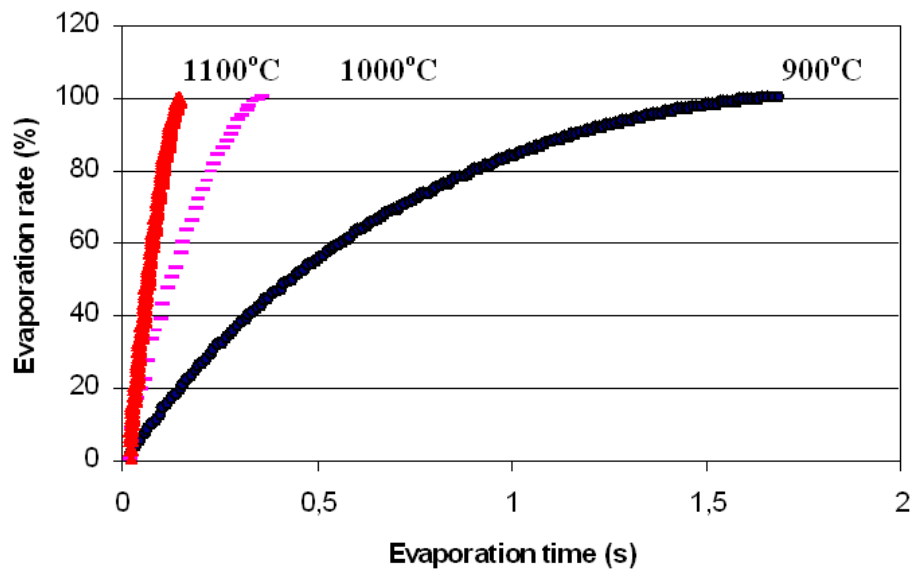
Maximum bulk KCl concentration:

Feed rate of kaolin/KCl mixture with 14.24 % KCl: 300 g/h

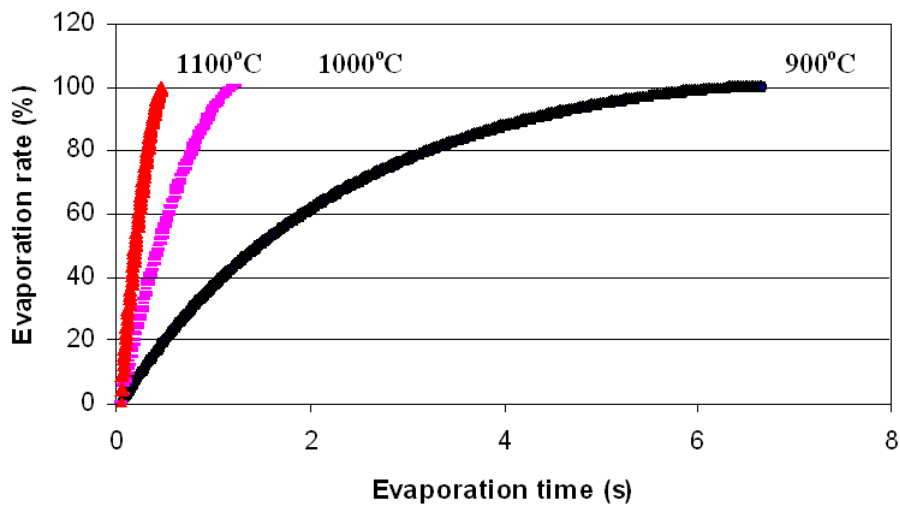
Total air flow: 60 NI/min

$$C_{KCl,bulk} = 10^6 \times \frac{14.24\% \times 5 \frac{g}{min} \times \frac{1}{74.55 \frac{g}{mol}} \times 22.4 \frac{NI}{mol}}{14.24\% \times 5 \frac{g}{min} \times \frac{1}{74.55 \frac{g}{mol}} \times 22.4 \frac{NI}{mol} + 60 \frac{NI}{min}}$$
$$= 3553 \text{ ppmv}$$

Saturated KCl concentration at 900, 1000 and 1100°C is 5685, 22743 and 72124 ppmv, respectively. Thus for the calculation of particle weight loss the bulk KCl concentration can not be neglected at least at 900°C.



Evaporation rate of 40 μ m KCl particle at different temperatures as function of time.



Evaporation rate of 75 μ m KCl particle at different temperatures as function of time.

Appendix B. Detailed analysis results for series 2 tests.

Table 1. KCl/kaolin mixture test.

Run No.	1	2	3	4	5	6	7	8
Temperature(°C)	1100	1100	1100	1100	1100	1100	1200	1300
Residence time(S)	1.07	1.07	1.07	0.54	0.77	1.22	1.07	1.07
K/Si input in mixture(molar ratio)	0.1	0.18	0.34	0.34	0.34	0.34	0.34	0.34
Total Al in collected sample (wt%)	18.4	18.6	17.9	16.7	17.5	16.6	18.2	17.6
Al-input in mixture (wt%)	19.3	18.6	17.2	17.2	17.2	17.2	17.2	17.2
Total Si in collected sample (wt%)	25.4	24.4	22.9	22.3	22.5	24.0	23.4	22.3
Si-input in mixture (wt%)	21.9	21.1	19.6	19.6	19.6	19.6	19.6	19.6
Total K in collected sample (wt%)	3.98	5.53	7.93	9.48	7.82	8.26	8.37	9.44
K_input_from kaolin (wt%)	1.27	1.22	1.13	1.13	1.13	1.13	1.13	1.13
K_input_from KCl (wt%)	2.05	4.00	7.47	7.47	7.47	7.47	7.47	7.47
Total K_input (wt%)	3.32	5.22	8.60	8.60	8.60	8.60	8.60	8.60
Total K in collected sample/Total K input (wt%)	119.91	105.92	92.20	110.22	90.92	96.04	97.26	109.70
Cl content in collected sample (wt%)	0.70	1.47	2.26	5.18	3.19	2.43	1.7	2.04
Cl_input in mixture (wt%)	1.86	3.63	6.77	6.77	6.77	6.77	6.77	6.77
Water soluble K in collected sample (wt%)	0.61	1.00	1.40	4.66	2.03	1.72	1.20	1.27
Water soluble K/total K in collected sample (wt%)	15.35	18.12	17.59	49.10	25.90	20.76	14.29	13.41
Water insoluble K in collected sample (wt%)	3.37	4.53	6.54	4.83	5.80	6.55	7.17	8.17
Calculated water insoluble K/total K (wt%)	101.50	86.73	75.98	56.10	67.38	76.10	83.37	94.99
Calculated soluble K/Cl molar ratio	0.79	0.62	0.56	0.82	0.58	0.64	0.64	0.56
KCl conversion from K content (%)	70.24	75.00	81.26	37.62	72.82	76.97	83.94	83.00
KCl conversion from Cl content (%)	62.37	59.50	66.62	23.49	52.88	64.11	74.89	69.87

Note:

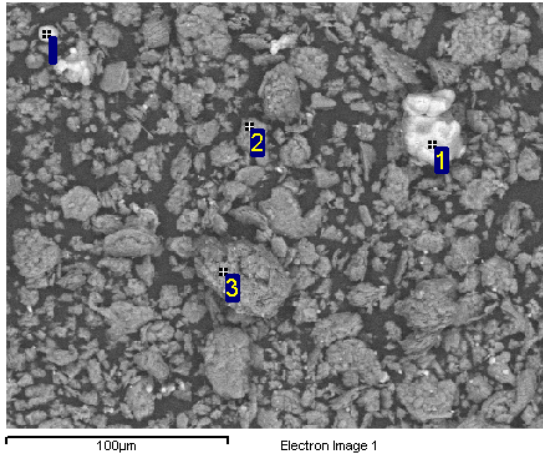
1. The elemental input in the mixture is calculated from the chemical analysis and weight fraction of kaolin.
2. KCl conversion calculated from K content: $100\% \times (1 - \text{water soluble K in reacted sample} / \text{K input from KCl})$
3. KCl conversion calculated from Cl content: $100\% \times (1 - \text{Cl in reacted sample} / \text{Cl input from KCl})$

Table 2. KCl/SAKLEI fly ash test.

Run No.	9	10	11
Temperature(°C)	1100	1200	1300
Residence time(S)	1.07	1.07	1.07
K/Si input in mixture(molar ratio)	0.34	0.34	0.34
Total Al in collected sample (wt%)	13.9	15.7	14.7
Al-input in mixture (wt%)	15.0	15.0	15.0
Total Si in collected sample (wt%)	17.6	20.4	18.7
Si-input in mixture (wt%)	19.4	19.4	19.4
Total K in collected sample (wt%)	11.9	9.53	10.05
K_input_from Saklei (wt%)	0.45	0.45	0.45
K_input_from KCl (wt%)	8.99	8.99	8.99
Water soluble K_input (wt%)	8.99	8.99	8.99
Total K_input (wt%)	9.44	9.44	9.44
Total K in collected sample/Total K input (wt%)	126.03	100.88	106.38
Cl content in collected sample (wt%)	11.50	9.15	8.00
Cl_input in mixture (wt%)	8.16	8.16	8.16
Water soluble K in collected sample (wt%)	11.15	8.32	7.66
Water soluble K/total K in collected sample (wt%)	93.70	87.35	76.21
Water insoluble K in collected sample (wt%)	0.75	1.21	2.39
Calculated water insoluble K/total K (wt%)	7.94	12.76	25.31
Calculated soluble K/Cl molar ratio	0.88	0.82	0.87
Calculated K evaporation from analysis (%)	3.36	8.42	21.60
Total Ca in collected sample (wt%)	3.59	3.27	3.57
Water soluble Ca in collected sample (wt%)	0.79	0.67	0.45
Ca_input in mixture (wt%)	2.89	2.89	2.89
Total Mg in collected sample (wt%)	0.10	0.06	0.08
Water soluble Mg in collected sample (wt%)	0.03	0.07	0.04
Mg_input in mixture (wt%)	0.50	0.50	0.50
Total Na in collected sample (wt%)	0.71	0.66	0.71
Water soluble Na in collected sample (wt%)	0.08	0.05	0.04
Na_input in mixture (wt%)	0.09	0.09	0.09

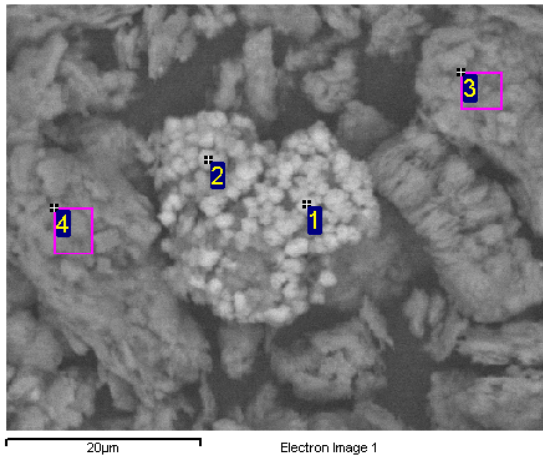
Appendix C. Detailed results from SEM-EDX analysis

1. KCl/kaolin mixture with K/Si molar ratio of 0.34, reacted at 1100 °C. residence time 0.54s.

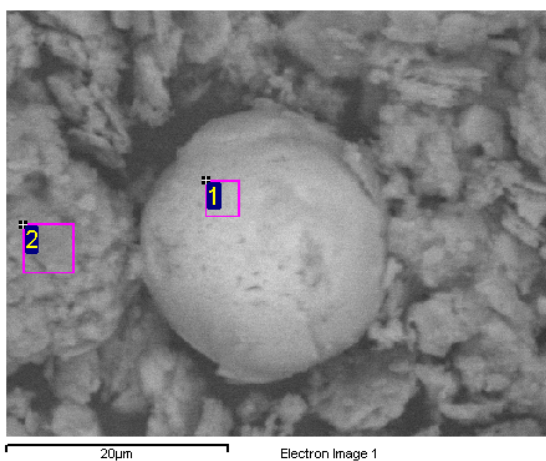


point	Al	Si	Cl	K
	mol%			
1	2.64	3.25	48.29	45.83
2	12.59	14.83	35.14	37.44
3	36.72	47.02	0.00	16.26

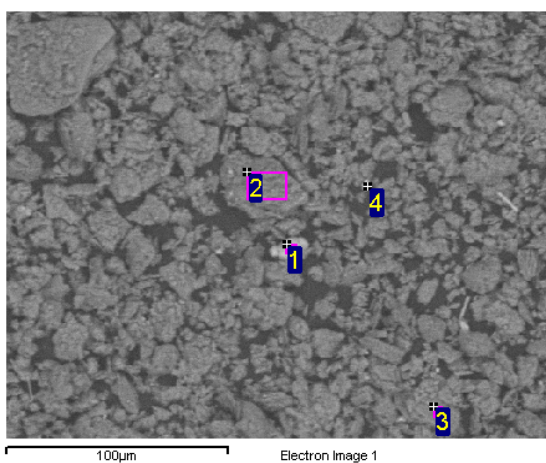
2. KCl/kaolin mixture with K/Si molar ratio of 0.34, reacted at 1100 °C. residence time 1.07 s



point	Na	Al	Si	Cl	K	Fe
	mol%					
1	0.00	7.45	7.89	41.08	43.58	0.00
2	0.47	10.52	12.87	36.76	39.38	0.00
3	0.00	36.19	46.39	2.48	14.16	0.78
4	0.00	34.43	45.06	3.72	16.80	0.00

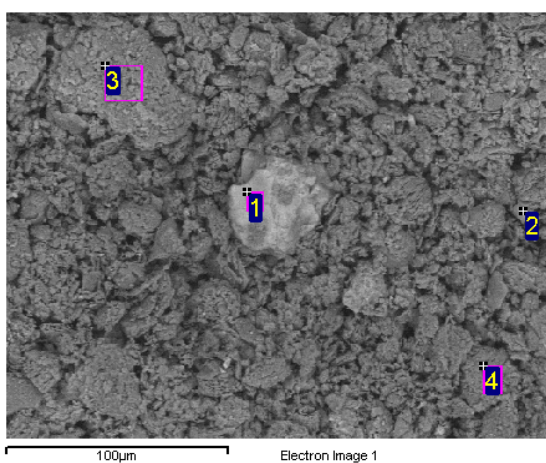


point	Al	Si	Cl	K	Fe
	mol%				
1	0.49	0.74	48.77	50.00	0.00
2	36.78	47.78	1.85	12.96	0.63

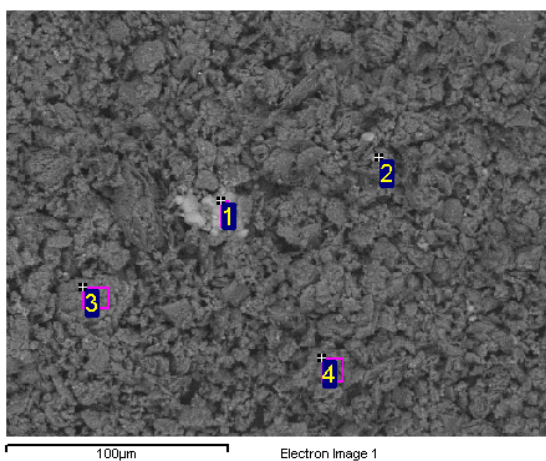


point	Mg	Al	Si	Cl	K	Fe
	mol%					
1	0.00	0.95	1.10	48.52	49.43	0.00
2	0.00	35.47	47.75	2.73	13.29	0.77
3	1.36	33.18	50.81	1.34	12.27	1.03
4	0.00	4.69	5.38	45.20	44.74	0.00

3. *KCl/kaolin mixture with K/Si molar ratio of 0.34. reacted at 1200 °C. residence time 1.07 s*

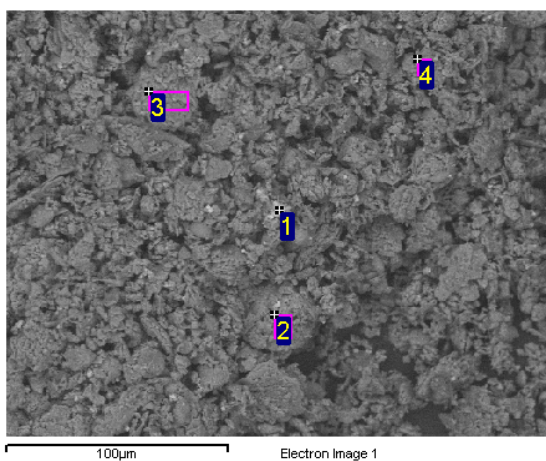


point	Al	Si	Cl	K
	mol%			
1	0.49	0.56	49.75	49.19
2	0.84	1.24	48.84	49.08
3	37.38	49.26	0.88	12.48
4	31.41	54.06	1.53	13.00

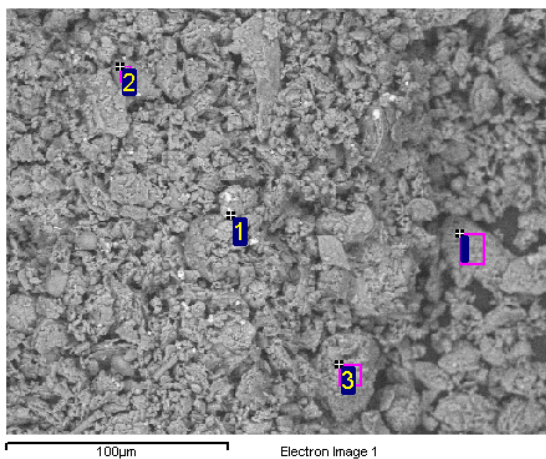


point	Al	Si	Cl	K
	mol%			
1	2.41	2.92	48.53	46.14
2	4.29	5.03	31.88	58.80
3	37.22	47.47	1.37	13.94
4	35.78	46.99	2.01	15.22

4. KCl/kaolin mixture with K/Si molar ratio of 0.34, reacted at 1300 °C. residence time 1.07 s

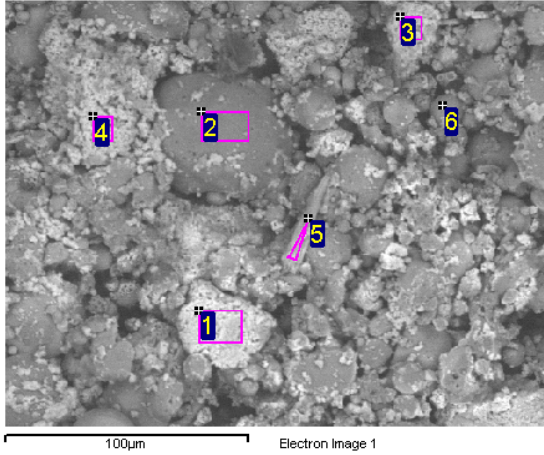


point	Al	Si	Cl	K	Fe
	mol%				
1	1.08	1.01	48.84	49.07	0.00
2	27.48	33.84	1.22	32.31	5.15
3	36.05	47.37	1.29	14.30	0.99
4	31.78	43.40	1.66	20.73	2.43

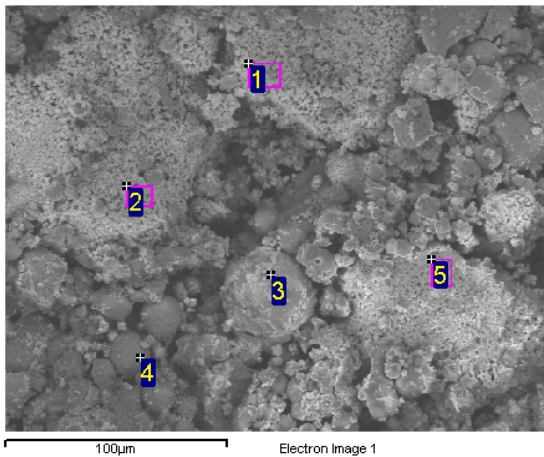


point	Al	Si	Cl	K	Fe
	mol%				
1	4.31	4.31	47.62	43.76	0.00
2	17.50	74.24	0.78	6.60	0.87
3	34.35	43.32	1.35	19.53	1.45

5. KCl/SAKLEI fly ash mixture with K/Si molar ratio of 0.34. reacted at 1100 °C. residence time 1.07 s



point	Na	Mg	Al	Si	Cl	K	Ca	Ti
	mol%							
1	3.02	0.26	1.43	1.66	50.12	41.28	2.66	0.00
2	0.00	0.51	40.95	49.17	1.06	4.65	2.59	1.07
3	0.00	0.00	0.64	0.85	55.57	42.94	0.00	0.00
4	1.73	0.43	0.91	1.03	52.14	44.01	0.00	0.00
5	0.00	5.87	5.51	6.29	40.15	4.41	37.76	0.00
6	0.00	0.13	41.80	52.68	0.69	2.93	1.27	0.50



point	Na	Fe	Al	Si	Cl	K	Ca	Ti
	mol%							
1	0.73	0.00	0.94	1.29	52.23	44.92	0.00	0.00
2	1.10	0.00	0.99	1.02	53.15	43.91	0.00	0.00
3	0.00	0.00	1.72	2.05	49.89	46.34	0.00	0.00
4	0.00	3.39	12.97	8.82	23.38	40.59	7.80	3.05
5	2.56	0.00	0.92	0.76	52.16	43.97	0.00	0.00

Appendix D. Description of models

1. Plug flow model considering intraparticle diffusion and kinetic

Conversion of KCl is calculated from single particle conversion and kaolin/KCl molar ratio. The model is developed by assuming reaction takes place in batch reactor since the results is identical to a plug flow reactor. Under the reaction temperatures applied in this work kaolin transfers to metakaolin.

Load of KCl: M (mol)

Kaolin to KCl molar ratio: MR

Load of kaolin: $M \cdot MR$ (mol)

Single cylindrical metakaolin particle weight: $m = \rho \cdot \pi \cdot R_p^2 \cdot L_p$ (g)

Molar amount of single metakaolin particle: $\rho \cdot \pi \cdot R_p^2 \cdot L_p / 222.14$ (mol)

Number of metakaolin particles in the flow: $n = M \cdot MR / (\rho \cdot \pi \cdot R_p^2 \cdot L_p / 222.14)$

Single metakaolin particle conversion after time t using updated KCl bulk concentration

X_{kaolin} molar amount of KCl captured by single particle:

$$2X_{metakaolin} \cdot \rho \cdot \pi \cdot R_p^2 \cdot L_p / 222.14 \text{ (mol)}$$

Potassium capture by all metakaolin particles:

$$n \cdot 2X_{metakaolin} \cdot \rho \cdot \pi \cdot R_p^2 \cdot L_p / 222.14 = (M \cdot MR / (\rho \cdot \pi \cdot R_p^2 \cdot L_p \cdot 222.14)).$$

$$2X_{metakaolin} \cdot \rho \cdot \pi \cdot R_p^2 \cdot L_p / 222.14 \text{ (mol)} = 2X_{mrtakaolin} \cdot M \cdot MR.$$

$$\text{KCl conversion: } X = \text{captured KCl} / \text{KCl input} = 2X_{metakaolin} \cdot M \cdot MR / M = 2MR \cdot X_{metakaolin}$$

2. Gas film control model

Conversion of KCl through reaction with a single kaolin particle:

$$k_g \cdot A \cdot C_{bulk} = \pi \cdot d_p^2 \cdot k_g \cdot C_{bulk} \text{ (mol/s)}$$

$$k_g = D \cdot Sh / d_p = 2D / d_p \text{ (m/s)} \text{ (Sh can be taken as 2 for small particles as shown in the KCl evaporation section)}$$

Metakaolin to KCl molar ratio: MR

KCl inlet: M (mol)

$$\text{Number of metakaolin particle: } n = MR \cdot M \cdot MW / (\pi d_p^3 \rho / 6)$$

Initial KCl conversion after a small time step dt :

$dX = dt \cdot n \cdot \pi \cdot d_p^2 \cdot k_g \cdot C_{\text{bulk},o} / M = 12 \cdot 222 \cdot 14 \cdot MR \cdot D \cdot C_{\text{bulk},o} \cdot dt / (d_p^2 \cdot \rho)$. where D is diffusion coefficient of KCl in nitrogen. Here the density is the density of pure metakaolin. 2510 kg/m³.

Then the bulk KCl concentration is updated: $C_{\text{bulk},o} = C_{\text{bulk},o}(1-X)$ and KCl conversion is integrated over time.

The calculation is then carried out to desired reaction time.

3. Kinetic model

Assuming KCl and kaolin are put in a batch reactor. we get

$dN/dt = k \cdot C_{\text{bulk}} \cdot V_p$. where V_p is the volume of kaolin particles

Metakaolin to KCl molar ratio: MR

KCl inlet: M (mol)

Volume of kaolin: $M \cdot MR \cdot MW_{\text{metakaolin}} / \rho$ (m³). Here the density is the density of pure metakaolin

Then the bulk KCl concentration is updated for each time step: $C_{\text{bulk},o} = C_{\text{bulk},o}(1-X)$ and KCl conversion is integrated over time.

$dX = dt \cdot k \cdot C_{\text{bulk},o}(1-X) \cdot M \cdot MR \cdot MW_{\text{metakaolin}} / \rho$

The calculation is then carried out to desired reaction time.